

RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division
of the American Chemical Society,
20th and Northampton Streets,
Easton, Pa.

Editor.....C. C. DAVIS
Associate Editor.....H. L. FISHER
Secretary-Treasurer.....H. E. SIMMONS

Vol. II

April, 1929

No. 2

CONTENTS

General Subjects

	Page
Rubber Division Activities.....	H. E. SIMMONS xxvii
New Books and Other Publications.....	xxviii
A Survey of Recent Literature on the Chemistry of Rubber.....	xxx

Reprinted Papers

Color Reactions of Rubber and Gutta-Percha. By F. KIRCHHOF.....	193
Some New Laboratory Work on Rubber. By A. A. SOMERVILLE and J. M. BALL.....	197
A Comparison of the Rate of Combination of Sulfur with Rubber and the Rate of Vulcanization. By E. R. BRIDGWATER.....	209
The Mechanism of the Reinforcement of Rubber by Pigments. By HARLAN A. DEPEW.....	216
Rubber as It Is Revealed by X-Rays. By GEORGE L. CLARK.....	225
The Evaluation of Carbon Blacks. By D. F. CRANOR and H. A. BRAENDLE.....	237
Technical Application of Antioxidants. By E. R. BRIDGWATER.....	243
Measuring Temperatures of Calender Rolls. By L. R. KELTNER.....	248
Goodyear Experience in Temperature Control of Mill Rolls. By R. W. MOORHOUSE.....	251
Contribution to the Thermochemistry of Rubber. By SIEGFRIED BOSTRÖM.....	259
A Thermodynamic Theory of Rubber Fillers. By LOTHAR HOCK.....	275

Entered as second-class matter May 12, 1928, at the Post-Office at Easton, Pennsylvania, under the Act of August 24, 1912.

Making Rubber Goods of Latex by Electro-Deposition. By PAUL KLEIN...	278
X-Ray Contributions to the Problem of Polymerization. By GEORGE L. CLARK.....	285
Rubber Structure Research and Its Bearing on the Elastic Properties of Colloids in General. By E. A. HAUSER.....	301
A New Physical Test for Vulcanized Rubber. By D. D. WRIGHT.....	308
Practical Method for Obtaining Dry Air for Humidity Control in a Rubber Laboratory. By F. S. CONOVER.....	318
Diffusion of Water through Rubber. By EARLE E. SCHUMACHER and LAWRENCE FERGUSON.....	323
Report of the Raw Rubber Specifications Committee.....	335

RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Anyone who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of \$4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of \$6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman.....ARNOLD H. SMITH, Rubber Service Laboratories
Vice Chairman.....STANLEY KRALL, Fisk Rubber Co.
Secretary-Treasurer.....H. E. SIMMONS, Municipal University of Akron
Executive Committee...H. L. FISHER, E. R. BRIDGWATER, S. M. CADWELL, C. W. SANDERSON, H. A. WINKELMANN.

Financial Statement

Balance on hand December 20, 1928 (last financial report)	\$1001.92	
Deposits.....	<u>1203.00</u>	\$2204.92
Disbursements:		
Translation.....	\$23.00	
Printing.....	39.38	
Stenographic services.....	22.13	
Refunds.....	51.00	
India Rubber World.....	65.00	
Supplies and postage.....	5.03	
Mack Printing Company.....	<u>250.26</u>	455.80
Balance in bank March 25, 1929.....		<u>\$1749.12</u>

H. E. SIMMONS, *Treasurer*

New Books and Other Publications

Le Caoutchouc. Étude économique et statistique. JOSE CARLOS DE MACEDO SOARES. 160 pages. A. D. Cillard, Paris, 1928.

Brazil is producing about the same quantity of rubber as in 1900, while the production of the world is at present over twelve times that of 1900. It is difficult for a Brazilian to view this situation complacently, particularly when he realizes that potentially Brazil can supply the entire world with its requirements. The author is distressed at the failure of his country to supply its rightful share of the rubber consumed, and in an enthusiastic spirit points out ways and means by which it may regain its supremacy in the production of rubber. He refers to the coffee industry as suggestive of the results which may be attained by systematic business and technical enterprise. He is led in his development of the subject into long discussions on the evolution of the rubber industry, the production of rubber in various places and at different times, the dependence of rubber production on the automobile and other industries, the economics of production, including control such as the Stevenson plan, and finally the attitude of the United States toward rubber-producing countries in view of its present economic imperialism.

As a source of technical information, the reader will find almost nothing, but as a bird's-eye view of the evolution of rubber as a world commodity and as an omen of the tremendous importance which Brazil may again assume in the future, the book is of cultural interest to those who do not restrict their interest in rubber to its chemistry and technology.—C. C. DAVIS.

[From *Industrial and Engineering Chemistry*, Vol. 21, No. 2, page 195 (1929).]

Guide to the Preparation of Plantation Rubber. Rubber Research Institute of Malaya. Planting Manual No. 1. B. J. EATON. 45 pages. Kuala Lumpur, 1928. Price, \$2.00.

The Malayan Rubber Research Institute has recently issued an official statement announcing that three types of publication will be used for the permanent records of research work conducted by the Institute. These will take the form of *Bulletins* issued at irregular intervals in connection with particular investigations, a *Quarterly Journal*, and *Planting Manuals* issued about once a year. The book under review is the first of the projected *Manuals*, and the first publication of the Institute.

In a foreword, Dr. Bryce points out that the Malayan Institute will be concerned with fundamental research in the major problems of the rubber-growing industry and also with the improvement of the details of estate practice. The *Manuals* are to be issued with the latter object in view in order to present the available information on the technic of cultivation and production in a readily accessible and permanent form.

The book falls into eight main sections: smoked sheet, pale crepe, sole crepe, lower grade crepes, other types of first grade rubber, packing, storage of chemicals, and samples for investigation. Field and factory operations are described, with precise reference to the numerous technicalities which make the difference between good and inferior products. In some respects the work is a revised and extended version of the author's previous discussion of the subject (F. M. S. Dept. of Agriculture, *Bulletin* No. 17, 1912), but the present text is limited strictly to sound and tried technic. Suggestions of a tentative or experimental character which have not yet proved of permanent worth are omitted.

The section on other types of first grade rubber includes sub-sections on slab rubbers, "sprayed" rubber, ammoniated latex, and latex concentrated by evaporation ("Revertex") and by centrifuging. Their inclusion emphasizes the rapid increase in specialized knowledge demanded of the planter. Appendices on the information required in making criticisms of estate difficulties, on *para*-nitrophenol as a mold preventive, and on the interpretation of vulcanization and other tests on rubber, offer further evidence of this specialization.

The value of books like the present in enabling planters to keep abreast of established scientific advances is obvious, and all the more so in view of the current need for increased efficiency and reduced costs.

[From *Transactions of the Institution of the Rubber Industry*, Vol. 4, No. 4, December, 1928.]

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the January 10 and 20, February 10 and 20, and March 10 and 20, 1929, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial and trade journals throughout the world.

The constitution of rubber. HEINRICH LOEWEN. *Kautschuk* 4, 163-4(1928).—It is considered that colloid-chem. research will not in itself solve the problem of the constitution and unique properties of rubber. Fundamental research on the org. chemistry of the rubber mol. is just as necessary, for it is unlikely that rubber is the only substance whose properties depend upon chem. constitution. The great difficulty in ascertaining the chem. constitution of rubber has been the fact that most of its derivs. are also amorphous and of mol. wts. of the same order of magnitude as rubber. The ozonides are about the only derivs. which can be converted into relatively simple compds. The present paper is a preliminary report on a scheme of research, the object of which is to obtain derivs. of rubber which will throw light on the structure of the latter. As a reagent, HCl was considered preferable to Br, because rubber-HCl is more stable than rubber bromide, and because a higher halogen content (with Br) involves more complicated decompns. Assuming rubber to contain the group— $\text{CH}_2\text{CH}:\text{CMe}.\text{CH}_2$, it is shown that with HCl, several *addn. reactions* are possible, with formation of various known compds., depending upon whether partial or complete satn. occurs, upon the part of the mol. where partial satn. occurs, and upon the subsequent character of the cleavage. Crepe (extd. with AcMe) in CHCl_3 was first treated with 0.5 the quantity of HCl gas calcd. for complete satn., after which it was ozonized. The ozonide soln. was then warmed to 70° with water, the HCl neutralized with CaCO_3 , the CHCl_3 evapd., more water added and distd. at 125-35° to 0.5 its vol. The distillate contained probably levulinic aldehyde, while the red-yellow aq. residue contained a light yellow *semi-solid*, which was sol. in EtOH and was not a rubber-HCl. This EtOH soln., after filtration, gave a *ppt.* partially sol. in dil. NaOH, the latter soln. giving in turn *ppts.* with acids, Ba salts and Pb salts. Extd. with Et_2O and evapd., the red-yellow aq. soln. (*loc. cit.*) yielded a light yellow *oil*, while the residual soln. from the extn. gave on evapn. a dark *oil*. This latter oil crystd. to a mixt. of 2 substances, which were sol. in EtOH, insol. in Et_2O and gave *ppts.* with sol. Pb or Ba salts. These various compds. have not been identified, but the expts. show that volatile and crystallizable derivs. can be obtained from rubber without subjecting the latter to very energetic reactions. C. C. D.

Improvement of the properties of rubber by a technical change in its microstructure. H. POHLE. *Gummi-Ztg.* 42, 2687-8(1928).—A large no. of photomicrographs in natural colors shows the relation between the stress-strain curves of vulcanizates and their microstructures, the curves depending upon the particle size and the state of dispersion of the "active" fillers. The particles which play a predominant role in the quality are of microscopic dimensions, and microscopic analysis will therefore show in what way particles of different sizes influence the stress-strain curves. The influence of particle size on the stress-strain curve can, however, be detd. only when the same substance is under consideration. Under these conditions it is possible to change the shape of a stress-strain curve from convex to concave or *vice versa* by the addn. of a small proportion of particles of a different size to a filler, *e. g.*, by the addn. of a small proportion of colloidal graphite to gas black. Sb_2S_3 , Sb_2S_3 , factice, mineral rubber and different grades of ZnO and C black can be identified by photomicrographic analysis. In the colloidal form, fillers usually show microscopically a granulation of a characteristic color, which enables the particles to be identified and their fineness estd. Thus under a magnification of 2000, C black shows a fine red-brown granulation, while lamp black and "Thermax" appear different enough to be distinguishable both with respect to

their identify and their fineness. A uniform appearance of this granulation would suggest uniform dispersion, but microscopic analysis shows that frequently this is not so. By alternate pressing and warming thin sections, it is possible to obtain microsections which split in a way similar to mica, giving lamellas less than 0.001 mm. thick which appear to have been under different tensions. Such a structure may be obtained in a particularly effective way by mixing on a mill pale crepe and crepe contg. gas black, under which conditions the laminated structure becomes finer with the time of milling; but regardless of the time of milling, the mixt. fails to become homogeneous, alternate lamellas of the 2 components remaining visible.

C. C. DAVIS

Coagulation phenomena in Hevea latex. VII. Phenomena in alkaline latex. OTTO DE VRIES AND N. BEUMÉE-NIEUWLAND. *Arch. Rubbercultuur* 12, 454-64 (1928). (In English 465-71); cf. *C. A.* 22, 698.—The power of coalse to coalesce flocks in B-mixt. is destroyed not only by heating, by disinfectants and by acidifying to the 2nd liquid zone (cf. *C. A.* 18, 482; 19, 419) but also by making the latex alk. Fresh undild. latex loses its coalescing power immediately by the addn. of 0.4 N NH_4OH or 0.04 N NaOH, and the addn. of 0.1 N NH_4OH or 0.35 N NaOH destroys its coalescing power in approx. 1 hr. Acidification of the mixts. shortly after addn. of the alkali only partly restores the coalescing power. Accordingly latex preserved in the ordinary way with NH_3 has lost its coalescing power. With the aq. ext. from coagulum obtained with EtOH, the limits at which the coalse is destroyed are at 0.15 N NH_4OH and 0.015 N NaOH. The coalse in exts. is destroyed at a limit of p_H 8, both with NH_4OH and with NaOH. Around this limit the coalescing power is lost gradually, and the larger the dose the more rapid is this loss. The acidity of latex, its content of NH_4MgPO_4 and other factors also influence these phenomena. Addn. of AcONa up to 10 g. per 100 cc. to dild. or undild. latex does not decrease the coalescing power, while the alky. increases only from p_H 6.4 to 7, i. e., fails to reach the limit of p_H 8 mentioned above.

C. C. DAVIS

Preserving latex with borax. N. BEUMÉE-NIEUWLAND. *Arch. Rubbercultuur* 12, 441-52 (1928). (Summarized in English 453).—Borax may be used as an anticoagulant, for which purpose 1.2-1.5 g. per l. of latex is recommended. As a preservative, at least 30 g. per l. must be used. With an addn. of 20-25 g. per l., decompn. of the latex is inhibited, but a layer of rubber seps. on the top and a marked odor of glue becomes evident, indicating that the latex has not been rendered completely stable. Latex contg. borax has a lower viscosity than the corresponding latex without borax. Rubber prepd. from latex preserved with borax dries more slowly than rubber made under the same conditions but without borax. When latex is treated with borax and then kept for different times before coagulation, the rate of vulcanization of the rubber is slower than the corresponding rubber without borax up to about 2 weeks of preservation before coagulating. After allowing latex to stand over 2 weeks before coagulation, the rate of vulcanization of the rubber increases again until it eventually approaches the normal rate. In a similar way, the viscosity of rubber from latex contg. borax is lower than rubber from latex without borax, provided that the rubber is coagulated within a few days after addn. of the borax. If the latex is kept a long time with borax before coagulation, the viscosity of the resulting rubber increases until it reaches that of rubber from latex contg. no borax. Rubber prepd. from latex contg. borax is more plastic than the corresponding rubber from latex without borax.

C. C. DAVIS

Chemical analysis applied to the selection of Hevea. A. W. K. DE JONG. *Arch. Rubbercultuur* 12, 472-501 (1928). (Summarized in English 502-3).—The expts. represent the beginning of a systematic attempt to develop a method for foreseeing the yield and the quality of rubber from a given *Hevea* tree. Extn. of the blades of leaves with C_6H_6 and detn. of the rubber content showed very little difference between trees with a high yield and those with a low yield. Rubber extd. in this way from the stalks contained only about 80% hydrocarbons and the product oxidized easily, in fact accelerated the oxidation of crepe rubber, resembling the product obtained by exposing rubber solns. in quartz vessels. From the acetone and alc. exts. of the leaves a cryst. substance which m. 278-80° was obtained. Antioxidants are also present in the leaves.

C. C. DAVIS

Extraction of gutta-percha leaf. A. W. K. DE JONG. *Arch. Rubbercultuur* 12, 540-55 (1928). (Summarized in English 556-7).—Gutta-percha cannot be obtained by mech. methods from fallen leaves. The latter have the highest content of gutta-percha, and so expts. were started to det. whether a relatively pure product can be obtained by extn. of the fallen leaves. In preliminary expts., the addn. of the antioxidant of rubber to trunk gutta and to leaf gutta increased the resistance of the former to heating up to 90-100° but not that of the latter. By extn. with EtOH and then with acetone (to which leaf antioxidant had been added), or by extn. with C_6H_6 to which

leaf antioxidant was added, a product was obtained which was extremely durable when heated up to 90–100°. When the powd. leaf was first boiled in AcOEt, and then extd. with C_6H_6 , a product was obtained which even without the addn. of an antioxidant was extremely durable when heated up to 90–100°. This indicates that the antioxidant is not extd. by AcOEt, though upon purification of the antioxidant ext. of the leaf by AcOEt, the greater part dissolved. When purified with acetone or EtOH, the C_6H_6 and benzine exts. of fallen leaves showed antioxidant power. Purification with AcOEt at normal temp. gave a product with little durability, and dry heating of the benzene ext., if already purified, gave a readily oxidizable product. For extn. on a large scale this method cannot therefore be used, but it is possible that a successful method would comprise purification of the powd. leaf with EtOH with addn. of antioxidant, and subsequent extn. with C_6H_6 or benzine contg. antioxidant.

C. C. DAVIS

Sodium fluosilicate [in the production of raw rubber]. N. H. VAN HARPEN. *Arch. Rubbercultuur* 12, 423–31(1928). (In English 432–40); cf. van Dillen, Knaus, Kraay and Riebl, *C. A.* 22, 2682; van Harpen, *C. A.* 22, 1928.—A comparison of crepes made with the use of HCO_2H and Na_2SiF_6 , resp., as coagulants showed that Na_2SiF_6 gives the better colored crepe. Where the differences were small and close comparisons had to be made, it was found that the Lovibond tintometer was especially good, 0.5 g. of rubber being dissolved in 10 cc. of xylene. The quality of the crepe made with Na_2SiF_6 was as satisfactory as that with HCO_2H , for though the viscosity was lower and the tackiness greater, these were not abnormal. The rate of vulcanization, tensile strength and slope were normal. Na_2SiF_6 can be used as a coagulant for rubber for sole crepe, the properties of the latter being fully as satisfactory as sole crepe made under similar conditions but with HCO_2H . Further expts. show that an appreciable loss of rubber is not to be feared when Na_2SiF_6 is used as a coagulant, in fact with latex with a 20% rubber content a higher final wt. may be obtained because of greater absorption of smoke. This greater absorption probably depends upon the greater softness of the coagulum obtained by coagulation with Na_2SiF_6 . The low susceptibility to molds of sheet rubber prepd. with Na_2SiF_6 , attributed by certain investigators to the influence of the Na_2SiF_6 , is probably a result of the greater absorption of disinfectant components in the smoke.

C. C. DAVIS

A new rubber dough and solution mixer. ANON. *India Rubber J.* 76, 536(1928).—A new mixer (made by Baker, Perkins, Ltd., Peterborough, England) is described and illustrated, the most novel features of which are a pair of horizontal blades sufficiently powerful to allow the use of unmilled rubber and a special feed pump which controls the quantity of solvent and its rate of addn. It is made in capacities of 22, 44 and 110 gals.

C. C. DAVIS

Proportion of sulfur to be added to diphenylguanidine mixtures. W. B. WIEGAND. *Kautschuk* 4, 156(1928).—Comments on a paper by Esch (cf. *C. A.* 22, 2492). The optimum proportion of S to be used in mixts. with diphenylguanidine as accelerator depends not only upon the general character of the mixt. but depends specifically upon the proportion of diphenylguanidine.

C. C. DAVIS

Proportion of sulfur to be added to diphenylguanidine mixtures. WERNER ESCH. *Kautschuk* 4, 157(1928).—A reply to Wiegand (cf. preceding abstr.).

C. C. DAVIS

Important observations on rubber mixtures containing gas and lamp blacks. WERNER ESCH. *Gummi-Ztg.* 43, 75–8(1928).—Various expts. are described which show the difference between gas blacks and lamp blacks in rubber mixts. The superiority of the gas blacks was so marked that it was possible to replace a considerable proportion of new rubber by reclaimed rubber and still have the quality of the mixts. contg. the reclaimed rubber and gas black as good as the corresponding mixts. with new rubber and lamp black. In a series of mixts. where new rubber was replaced progressively by reclaimed rubber and the other ingredients, including the gas black, altered so that theoretically the same formula was maintained, the quality of the vulcanized mixts. became progressively poorer as the reclaimed rubber content increased.

C. C. DAVIS

The two accelerator effect. E. ANDERSON. *Trans. Inst. Rubber Industry* 4, 194–7(1928).—A review and discussion of papers by Naunton (*C. A.* 20, 3098), Martin and Davey (*C. A.* 17, 2203), Dinsmore and Zimmermann (*C. A.* 20, 1004) and Whitby and Cambron (*C. A.* 17, 3808), and patents of Weiss (U. S. Patents 1,521,739 and 1,546,876; cf. *C. A.* 19, 909, 2886) and Murrill (U. S. Patents 1,436,894 and 1,453,515; cf. *C. A.* 17, 652, 2204).

C. C. DAVIS

The manufacture of reclaimed rubber. N. BAN. *Kautschuk* 4, 193–4(1928).—A review, dealing with the present economic situation and methods of judging the quality of reclaimed rubber.

C. C. DAVIS

The development of rubber reclaiming since the war and its importance in the

economics of rubber. II. PAUL ALEXANDER. *Gummi-Ztg.* 42, 2847-8(1928); cf. C. A. 22, 4870.—A general discussion, dealing chiefly with production. C. C. DAVIS

Heat transmission. COLIN MACBETH. *Trans. Inst. Rubber Industry* 4, 137-47 (1928).—A review and discussion dealing with the importance of heat transmission in the rubber industry, including the part it plays in softening rubber preparatory to washing, washing rubber, drying washed rubber, masticating rubber, mixing, calendaring, spreading and vulcanization by various methods. A general discussion follows the paper. C. C. DAVIS

The absorption of light by stretched and by unstretched rubber and by isoprene. M. KRÖGER AND H. STAUDE. Univ. Leipzig. *Gummi-Ztg.* 43, 22, 24(1928); cf. C. A. 22, 3066.—The absorption of ultra-violet light by isoprene, isoprene rubber, unstretched and stretched raw and vulcanized rubber was measured by means of a quartz spectrograph to ascertain in what way the absorption of light is dependent upon the state of tension. In all cases the transparency of the stretched rubber samples was greater than that of the unstretched samples, especially with stretched membranes. The transparency of artificial rubber was greater than that of isoprene of the same thickness. Vulcanized rubber had very little transparency. The transparency was judged by the beginning of continuous absorption, not by individual absorption bands. The transparency of stretched raw or slightly vulcanized rubber membranes to ultra-violet light makes possible the manuf. of rubber lenses for ultra-violet radiation, in which case the lenses could be made as a cell contg. water or alc. C. C. DAVIS

Standard methods of analysis of rubber goods. A. E. LEIGHTON. *Australia Dept. of Defence Munitions Supply Board*, May 1926, 11 pp.—A procedure which involves standard methods is outlined for the analysis of rubber goods, including the prepn. of the sample, and detn. of the AcMe, CHCl_3 and alc. KOH exts., free S, total S (inclusive and exclusive of BaSO_4), ash, insol. ash, Pb, Sb, Sb in ash, Fe and Al, Zn, Ca and Mg, Mg, S in ash, BaSO_4 , BaCO_3 and rubber hydrocarbons. C. C. DAVIS

The manufacture of hard rubber dust. MAX RATHKE. *Gummi-Ztg.* 42, 2688-9 (1928).—A description of present developments. C. C. DAVIS

Process for rubberizing fabrics containing copper and manganese. ERICH WURM. *Gummi-Ztg.* 42, 2476-7(1928).—The patented process of Esch (cf. German Patent 461,134) has no practical importance, and may lead to disastrous results in manuf. C. C. DAVIS

Process for rubberizing fabrics containing copper and manganese. WERNER ESCH. *Gummi-Ztg.* 42, 2477-8(1928).—An answer to Wurm (cf. preceding abstr.). C. C. DAVIS

Process for rubberizing fabrics containing copper and manganese. ERICH WURM. *Gummi-Ztg.* 42, 2580-1(1928).—Answer (cf. preceding abstr.). As judged by tests in air at 70°, rubber vulcanized with tetramethylthiuramdisulfide deteriorates rapidly if treated with Cu salts before vulcanization, but if treated after vulcanization their deterioration is normal. C. C. DAVIS

Molded rubber goods. R. CLARK. *Trans. Inst. Rubber Industry* 4, 186-9(1928).—A discussion of current problems. C. C. DAVIS

Rubber as a floor covering. J. KIRKWOOD. *Trans. Inst. Rubber Industry* 4, 148-60(1928).—A general review and discussion of present developments, including the various ingredients used and their characteristic effects, and the methods of manuf. of different types of flooring. A general discussion follows the paper. C. C. D.

Some experiments on the manufacture of rubber road blocks. J. G. FOI AND F. C. VAN HEURN. Gov. Rubber Inst., Lab. Building Materials and Lab. Tech. Botany, Delft. *Bull. Rubber Grower's Assoc.* 10, 608-20(1928).—A new type of paving block is described which consists of a base of hard rubber, which may contain stone or sand, on which is superposed a resilient cap for the wearing surface. This cap may be vulcanized on the hard base by an intermediate semi-hard layer. The base material can be made by addn. of the stone to the uncured mixt. or by the Cresson method, using latex (cf. Brit. Pat. 191,474; C. A. 17, 3084). Various phys. tests of blocks made by different methods and of different compns. are described. The use of ordinary rubber mixts. instead of latex is preferable because (1) the drying operation is avoided; (2) more nearly homogeneous mixts. are obtained; (3) ingredients impossible to use in latex can be used, and (4) low-grade rubbers can be used. Typical formulas for the base, intermediate and surface layers which have given particularly good results are shown, and the technic for the construction and vulcanizing is described. C. C. D.

Rubber solvents, varnishes and coatings. R. ASSMAN. *Farbe u. Lack* 1928, 396, 411, 426-7.—Among the newer solvents for rubber are ethylene dichloride and tetrachloroethane. When 100 g. rubber are treated with 2.5 l. solvent, ethylene dichloride, tetrachloroethane and chloroform dissolve 99.5, 75.6 and 74.9%, resp. Hydrogenated

naphthalenes are relatively cheap and several formulas using them are given. Their chief advantage are favorable evapn. rates. A typical formula is 1 kg. of rubber fused in 2 kg. of rosin, to which are added 1 kg. of linseed oil and 1 kg. of tetralin, decalin or hydroterpin. A short review of English and German patents of products similar to "Thermoprene" is given. G. G. SWARD

The question of priority for the discovery of thermoplastic products from rubber, which resemble gutta-percha, balata and shellac, and their systematization. F. KIRCHHOF. *Kautschuk* 4, 142-9(1928).—A crit. review of the literature shows that the gutta-percha or shellac-like products obtained by Fisher from raw rubber by treatment with H_2SO_4 and sulfonic acids (cf. *C. A.* 21, 195; 22, 887, 2291) are essentially the same products which have previously been described by Harries (cf. *C. A.* 14, 1908) and by K. (cf. *C. A.* 15, 960; 16, 1885; *Kautschuk* Jan., 1926; Austrian Patents 90,775 (1921) and 93,480(1922)). Priority for the discovery of sulfo-rubbers is therefore with the German investigators. From the technical point of view the application of these substances (cf. Canadian Patent 256,567 (1925); U. S. Patent 1,605,180 (1926)) represents important progress, since the use of solvents is avoided. Thermoplastic substances in general are discussed, an attempt being made to classify these substances in 4 groups, according to their method of prepn. and the reagent used: (1) *sulfo-cyclorubbers*, comprising the H_2SO_4 -rubbers of Harries and of Kirchhof and the sulfonic acid-rubbers (thermoprenes) of Fisher; (2) *thermocyclorubbers*, comprising the mono-cyclorubber of Harries and the hydro-cyclorubber and the poly-cyclorubbers of Staudinger; (3) *photo-cyclorubbers* of Porritt and of Asano, and (4) *contact-polymer rubbers*, comprising the metallic halide-rubbers of Bruson and the Cl_2CCO_2H -rubber of the B. F. Goodrich Co. The methods of prepn., phys. and chem. properties and probable chem. constitution of these substances are tabulated. C. C. DAVIS

Pressure vulcanization. F. H. AMENDE. *Trans. Inst. Rubber Industry* 4, 170-80 (1928).—A general review and discussion dealing with the historical aspects and with different types of vulcanizers. Diagrams and graphs are included. A general discussion follows the paper. C. C. DAVIS

Vulcanization problems. ALFRED A. PERKS. *Trans. Inst. Rubber Industry* 4, 123-36(1928).—A review and discussion dealing with the dispersion of S in rubber, temps. used for vulcanizing, thermal characteristics of vulcanization, operation of vulcanizers, conditions to be satisfied during vulcanization, curing in different types of vulcanizers, varying degrees of cure depending upon the size of the product, and times of vulcanization. A general discussion follows the paper. C. C. DAVIS

The vulcanization of rubber. NICHOLAS BACON. *India Rubber J.* 76, 459-64, 504-7, 542-5(1928).—See *C. A.* 22, 3804. C. C. DAVIS

The vulcanization of rubber with metallic sulfides and an ultra-accelerator. TAKEJI YAMAZAKI. *J. Soc. Chem. Ind. Japan* 31, 165B(1928); *Gummi-Zig.* 43, 190.—The expts. deal with the influence of ZnS , $(NH_4)_2S$, PbS , CdS , Al_2S_3 and As_2O_3 on the vulcanization of mixts. contg. an ultra-accelerator. It was assumed that the presence of an ultra-accelerator would, in conjunction with the small proportion of free S in the sulfide, be capable of inducing vulcanization. Seven mixts., contg. besides smoked sheets 100, and diethylaminodiethyldithiocarbamate 2, the following quantities of ZnO and sulfide, were prepd.: (1) ZnO 30; (2) ZnO 10, ZnS 20; (3) ZnO 20, $(NH_4)_2S$ 10; (4) ZnO 10, PbS 20; (5) ZnO 10, CdS 20; (6) ZnO 10, Al_2S_3 20; (7) ZnO 10, As_2O_3 20. The mixts. were heated 30 and 110 min. at 3 atms. Mixts. (1), (3) and (6) were not cured at all, mixts. (2) and (4) were partly cured, and mixt. (5) was definitely cured. Of the sulfides which had led to a certain degree of cure, the ZnS contained 2.33% free S, PbS 0.02% free S and CdS 1.60% free S. When the CdS was first extd. with acetone, the vulcanizate had extremely poor phys. properties. Conclusion: The phys. properties of the 6 vulcanizates depended chiefly upon the proportion of free S in the metallic sulfides and only to a small extent on the metallic sulfide itself. The samples of mixts. contg. a sulfide which were thoroughly cured contained about the same proportion of free S as mixt. (1) contg. no sulfide, though their phys. properties were different. C. C. DAVIS

The discoloration of zinc oxide during vulcanization. J. A. ROBERTSON. *Trans. Inst. Rubber Industry* 4, 190-3(1928).—Experience has shown that when ZnO is darkened by H_2S it also darkens during vulcanization, but no systematic expts. on this problem are on record. This induced a closer examn. of the problem. Samples of ZnO contg. 0.16, 0.20 and 0.013% PbO , resp., all darkened to the same extent when exposed to H_2S or when heated in a rubber-S mixt. After extn. with water and drying, the first 2 samples darkened still more, whereas the 3rd sample was unaffected. Pure $PbSO_4$ was, when dry, unaffected by H_2S , but when moist it was darkened, probably because of the equil. reaction: $PbSO_4 + H_2S \rightleftharpoons PbS + H_2SO_4$.

in which case removal of the H_2SO_4 would result in complete conversion of the PbSO_4 . Two intimate mixts. of ZnO and PbSO_4 : (1) a thin paste dried, and (2) a dry-ground mixt., were each treated with H_2SO_4 . Only mixt. (1) darkened, probably because while wet the following reaction takes place: $\text{PbSO}_4 + \text{Zn}(\text{OH})_2 \rightleftharpoons 2\text{ZnSO}_4 + \text{PbO} \cdot \text{H}_2\text{O}$. The same relative effects were obtained after the mixts. had been ignited. Samples of basic Pb sulfate were darkened by H_2S . ZnSO_4 is very difficult to ext. from ZnO , suggesting that it is not present as such, but is formed by the water from $\text{Zn}(\text{OH})_2$ and PbSO_4 . Mixts. of ZnO and PbSO_4 and of ZnO and PbO (in the same proportions) were brought to equil. in water. The filtrate from the ZnO - PbO mixt. contained considerable Pb, whereas that from the ZnO - PbSO_4 mixt. contained almost none. Absence of Pb in filtrates from samples of com. ZnO depends therefore upon the fact that after treatment with water it is present as basic Pb sulfate and not as PbO . The expts. indicate that darkening of ZnO by H_2S results from the actions of the latter on basic Pb sulfate, and that in com. ZnO the Pb is present chiefly as PbSO_4 , with traces of basic Pb sulfate and PbO . By treatment of com. ZnO with water, PbSO_4 is converted into basic Pb sulfate, which is darkened by H_2S . This change is so easily brought about that exposure of com. ZnO to air soon makes it susceptible to darkening by H_2S in virtue of the atm. moisture. C. C. DAVIS

The effect of flour in rubber mixtures vulcanized with sulfur. RUDOLF DITMAR. Kautschuklaboratorium Graz. *Gummi-Ztg.* 43, 191(1928).—Expts. show that various flours, including wheat, rye, barley, oat, corn, buckwheat, rice, bean, pea and potato flour, are excellent plasticizing agents, their plasticizing power depending upon the particular flour and its fineness. As a result, flours facilitate the mixing of fillers, particularly high proportions of gas black. They are suitable for various mixts. provided they are not vulcanized at too high a temp., decompn. of the flour occurring above a certain range. This renders ultra-accelerators particularly useful when flour is used. The unfavorable effect of flours on the aging of vulcanized mixts. can be completely overcome with preservative agents (antioxidants). Flour is unsuitable for use in mixts. vulcanized with S_2Cl_2 . C. C. DAVIS

Dispersoidological investigation of latex. P. P. VON VEIMARN. *Kolloid-Z.* 46, 217-23(1928).—See C. A. 22, 4872. E. H.

Investigation on rubber prepared from primary and tertiary latex cream according to the Utermark patent. W. SPOON. *Arch. Rubbercultuur* 12, 596-603(1928). (Summarized in English 604).—The prepn. and drying of crepe from ammoniated primary and tertiary latex cream were investigated. The tertiary cream was obtained by centrifuging the primary cream twice, each time after diln. with water. Samples of crepe were prepd. in Holland from the primary and from the tertiary cream to det. the changes which they might undergo during a sea voyage. Rubber from primary and tertiary cream dried very slowly, while the chem. compn. of the former indicated a low proportion of non-rubber components and the chem. compn. of the latter a still purer rubber. The rate of vulcanization of these rubbers was abnormally slow, especially with tertiary rubber, while the quality after vulcanization was abnormally poor. Centrifuging the primary cream twice purified the rubber to some extent but did not improve the phys. quality. C. C. DAVIS

Investigations on Utermark cream and on rubber prepared therefrom. Comparison with some other rubber types. W. SPOON. *Arch. Rubbercultuur* 12, 576-93(1928). (Summarized in English 594-5).—*Hevea* latex concd. while fresh by the Utermark method (cf. British pat. 218,635) gave cream which contained 54-5 g. of dry rubber per 100 cc. of cream. Crepe rubber prepd. from fresh cream and from cream preserved with NH_3 was compared with crepe prepd. by ordinary methods from fresh latex and from latex preserved with NH_3 and with crepe from fresh underlatex. Crepe from cream was nearly white; that from underlatex was yellow. Crepe from cream preserved with NH_3 required twice as long to dry as crepe from normal latex preserved with NH_3 (cf. Stevens, C. A. 21, 2077). Rubber from cream contains a very low content of serum substances, whereas rubber from underlatex contains a considerable content. The phys. and chem. properties of crepe from underlatex resemble those of rubber prepd. by partial coagulation (cf. de Vries, C. A. 11, 2625), and the properties of crepe from cream resemble those of crepe from the residual liquid. Aging tests were carried out by heating at 70° in air, the change in wt. and in acetone ext. being detd. Rubber from cream was inferior in its aging properties to rubber prepd. in the ordinary way, which agrees with similar expts. by Stevens. Cured with S alone, rubber from cream vulcanized more slowly than did rubber prepd. in the ordinary way. Rubber from cream had a smaller capacity for water absorption than ordinary rubber. C. C. D.

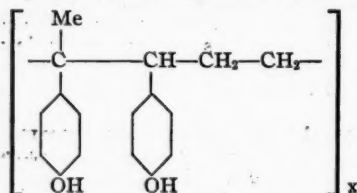
Determination of the specific gravity of rubber mixtures. ST. REINER. *Gummi-*

Zig. 43, 135(1928).—A method is recommended which involves cutting out a small sample, measuring its dimensions and wt. and thence calcg. the d. C. C. D.

Determination of the specific gravity of rubber mixtures. L. STOLL. *Gummi-Zig.* 43, 252(1928).—The methods for detg. d. as described by Reiner (cf. preceding abstr.) are impractical. It is best to follow standard methods, such as weighing in air and then in water, or the Mohr procedure. C. C. DAVIS

The absorption of the vapors of liquids by rubber. STEPHAN REINER. *Kautschuk* 4, 210-5(1928).—The possibility that rubber might be used in place of active powders as an absorptive agent for the recovery of volatile solvents led to expts. to det. at what rate and to what extent rubber absorbs such vapors at room temp. The app. and technic devised, which are described and illustrated in detail, allowed the measurement of the absorption of any vapor by rubber at const. temp. The rubber was purified by soln. in C_6H_6 and reprecip. with EtOH, and was finely divided to present a large surface area, and was then exposed to the vapor under the very carefully controlled conditions described. Data are tabulated for the continuous absorption of C_6H_6 vapor at 25° by rubber over a period of 700 hrs. These results show a rate of absorption which is relatively slow and progressive, no approach to equil. being evident even after 700 hrs. This is shown by the following values drawn from the results, the data giving the hrs. of exposure and the % C_6H_6 absorbed: 1, 0.2; 5, 0.37; 25, 1.07; 50, 1.80; 75, 2.62; 100, 3.24; 200, 5.46; 300, 7.10; 400, 9.30; 500, 12.10; 600, 13.50; 700, 16.10. At the end of 700 hrs., the rubber was sticky and swollen and with all indications that absorption would have continued progressively. C. C. DAVIS

Color reactions of rubber and gutta-percha. F. KIRCHHOFF. *Kautschuk* 4, 190-2 (1928).—A crit. review and discussion of a paper by Pauly (cf. C. A. 22, 1703), with the inclusion of new data. Like concd. H_2SO_4 , Cl_3CCO_2H isomerizes rubber (cf. C. A. 23, 307), and since moreover Cl_3CCO_2H gives characteristic color reactions with other unsatd. cyclic hydrocarbons, the Chugaev-Godoletz and allied reactions probably involve a transitory addn. of Cl_3CCOC_2H (or H_2SO_4) with formation of cyclorubber, which as a result of the colloidal state shows an intense coloration. By dissolving the product in water, the rubber isomer seps. in flocculent form. The appearance of these colors is not, therefore, a proof of the original existence of a ring structure in the rubber hydrocarbon (cf. Pauly, *loc. cit.*), but only of cyclization or rearrangements within the rubber mol. The comparatively great tendency of the rubber hydrocarbon toward cyclization is accordingly responsible for the color changes. Much more characteristic and significant is the color reaction of rubber dibromide noted by Weber (cf. Ber. 33, 791(1900)). Since phenolic ethers do not react with rubber dibromide, it was concluded by W. that the H atom of the OH group, and not the *p*-H of the Ph group, reacts with the Br, but this was disproved by Fisher, Gray and McCollm (cf. C. A. 20, 1987). It is therefore probable that hydroxyphenyl derivs. of hydorrubber of the constitution:



are formed (cf. Geiger, C. A. 21, 4093), which will also explain their soly. in alkalis. In the absence of catalysts, blue or red-violet fusion mixts. are formed which are stable for several days, but which change color when dissolved in org. solvents. The violet color of fusion mixts. of rubber or gutta-percha dibromide is a typical dispersive color reaction which depends upon the particle size, while the latter depends in turn upon the concn., temp. and occurrence of secondary reactions. Natural impurities in rubber therefore play a part and alter the color obtained with pure reagents. The Weber reaction can be utilized for the detection or identification of rubber or gutta-percha. Ext. a few centigrams of finely divided sample with acetone, swell or dissolve in CCl_4 , brominate in this soln., suspend a few mg. of bromide in 2-3 cc. of CCl_4 , add 1-2 cc. of very concd. PhOH (or the corresponding quantity of cryst. PhOH), warm to eliminate CCl_4 , and heat until the PhOH begins to boil. If rubber or gutta-percha is present, the characteristic blue or red-violet color appears. For further identification, dissolve a few drops of the fusion mixt. in an org. solvent ($CHCl_3$, Et_2O or Ac_2O) and note the color. About 6 mg. of gutta-percha bromide (from Tjipetir gutta-percha), i. e., about 2 mg. of gutta-percha hydrocarbon, in 10 cc. of $CHCl_3$ gave a distinct blue-violet color, so

even 0.2 mg. of rubber hydrocarbon can be detd. by this method. The reaction is applicable to hot- and cold-vulcanized rubber. With hexahydrophenol and phenetole there is no definite color reaction. The following data give the color of the dibromides, of the PhOH fusion mixts. and of their solns. in CHCl_3 , CCl_4 , Ac_2O and Et_2O , resp.: *pure rubber* (crepe), yellowish white, blue-violet, blue-violet, blue-violet, reddish yellow, yellow; *pure gutta-percha* (Tjipetir), white, blue, blue, blue-violet, reddish yellow, yellow; *oxidized gutta-percha*, yellowish white, carmine, carmine, carmine, reddish yellow, yellow; *synthetic rubber H*, yellowish white, cherry-red, cherry-red, cherry-red, —, yellow; *sulfocyclorubber*, yellow-brown, carmine, cherry-red, cherry-red, —, yellow; *Cl₃CCO₂H-rubber*, light yellow, reddish brown, reddish brown, reddish brown, —, yellow; *rosin oil*, light brown, reddish brown, reddish yellow, reddish yellow, —, brown; *rosin*, light brown, reddish yellow, reddish yellow, reddish yellow, —, brown. Heated with pyrogallol, rubber dibromide gives a cherry-red color, and with resorcinol a dark orange-red color. Like the PhOH mixts., these fusion mixts. give with alc. alkalis, intense yellow-brown solns. (alkali salts of the corresponding hydroxyphenylhydrorubbers). None of these fusion mixts. exhibits such a characteristic color as the PhOH products of rubber, gutta-percha and balata dibromides. C. C. DAVIS

The direct agglomeration of waste soft rubber and the manufacture of soles. L. GRAFFE. *Caoutchouc & gutta-percha* 25, 14186-7(1928).—As ordinarily encountered, the tendency of fresh surfaces of unvulcanized rubber to adhere and the lack of such tendency in vulcanized rubber depends upon the temp. and pressure, vulcanization merely changing the limits between which adhesion may be obtained. It is possible by the use of sufficiently high pressures and suitable elevated temps. to bind finely divided vulcanized waste rubber together into a compact mass, and thus obtain useful products directly, such as soles (cf. French patents 338,945(1903); 361,300(1905); English patents 12,454(1906); 28,267(1907)). The process may be made continuous, the ground material passing to heated hydraulic presses. Soling made in this way has shown tensile strengths of 0.35-0.40 kg. per sq. mm. and elongations of 150-250% with good resistance to abrasion. C. C. DAVIS

The resistance of rubber to compression. RAFFAELE ARIANO. *Nuovo Cimento*, [N. S. V.] 3, 77-107(1928); cf. C. A. 20, 3362; 22, 2081.—A. has explored mathematically the compression curves of rubber of different degrees of vulcanization, and the relation between variation in vol. and the Joule effect and Poisson's coeff. The Poisson coeff. for stretching is never greater than 0.5, but for compression varies from 0.5 to infinity. The expression for work of deformation has a logarithmic form. L. T. FAIRHALL

Jelutong. C. D. V. GEORGI. *Malayan Agr. J.* 16, 204-11(1928).—There are several reasons which may account for the tendency of jelutong from certain sources to oxidize to a brittle resin (cf. C. A. 22, 2078), among which are contamination with harmful metallic salts or alkalis. Expts. were therefore undertaken to det. whether the addn. of salts to jelutong latex would result in oxidation and resinification. FeSO_4 , FeCl_3 , CuSO_4 , MnSO_4 and MnCl_2 were added in sep. expts. to latex and the latter was then coagulated with AcOH . In control tests, latex was coagulated without the addn. of a salt. The coagula were then treated in the usual way and examd. after 6 months. Fe and Cu salts induced oxidation, whereas Mn salts only favored the growth of molds. With 0.01-0.02 g. of Fe per 100 cc. of latex, the jelutong oxidized considerably during 3 months of storage. Mn compds. have consequently a far different effect on jelutong than their effect on rubber. In further expts. fresh coagulum was extd. with boiling water, was then soaked in 1% aq. FeSO_4 , FeCl_3 , CuSO_4 , $\text{Cu}(\text{OAc})_3$, MnSO_4 , MnCl_2 , NaOH and KOH and finally was pressed into blocks, dried and stored for 6 months. Under these conditions the metallic compds. had little or no effect. Jelutong latex from Kedah differs in compn. from latex from the local forest reserves of Malay, expts. with the former showing no tendency to oxidize whether or not the jelutong had been extd. with boiling water, and whether or not it had been coagulated with AcOH , HCO_2H , H_2SO_4 , K alum or Na_2SiF_6 . Addn. of FeCl_3 to the latex, however, resulted in rapid oxidation. Addn. of NaCl (0.1 g. per 100 cc. of latex) had no influence on the aging. Kedah latex coagulated with alc. gave a product with no tendency to oxidize, but when the jelutong was creped and then blocked, oxidation ensued. C. C. DAVIS

The valuation of jelutong. C. D. V. GEORGI. *Malayan Agr. J.* 16, 220-33(1928); cf. preceding abstr.—Definite standards should be established for the manner of sampling, examn. and testing jelutong. Present methods for detg. the moisture content are unsatisfactory, since the water present in a block is unevenly distributed. A crit. survey of present methods of detg. water, with expts. on the development of a better method, shows that good results can be obtained by weighing the whole block, cutting into pieces, creping the latter, drying the crepes superficially, weighing, removing a part of each sample, repeating the process of creping, drying and removing a propor-

tionate part, creping finely, drying for 10 hrs. at 40°, cooling, weighing, removing an aliquot part and drying to const. wt. Jelutong has a tendency to gain weight when heated more than 6 hrs. at 100°. It darkens considerably, acquires an odor suggesting decompn., and probably both absorption of O and decompn. take place simultaneously, the former more rapidly than the latter. Data on moisture detns. of jelutong from various sources are given. C. C. DAVIS

Factors in the evaluation of vulcanized rubber mixtures. WERNER ESCH. *Kautschuk* 4, 215-22(1928).—A general discussion dealing with modern methods of compounding, with the object of showing the phys. quality obtained with different types of rubber mixts. The argument is supported by quant. data on the phys. quality obtained with various formulas, phys. tests before and after aging being given to show that it is impracticable to judge the phys. quality of rubber mixts. by the content of rubber and other ingredients. C. C. DAVIS

Is vulcanization a chemical phenomenon? PAUL BARY. *Rev. gén. caoutchouc* 5, No. 45, 3-7(1928).—A crit. review and discussion of recent work by Bacon (cf. C. A. 22, 3804). The expts. do not disprove the existence of "giant" mols., for the swelling of lyophilic colloids, particularly rubber, involves depolymerization and solvation (cf. Bary, C. A. 21, 670, 1911) with formation of mols. small enough to peptize. No explanation of vulcanization with very small proportions of S in the presence of an ultra-accelerator is offered. Difficulties in explaining the degree of polymerization of raw and of vulcanized rubber and the continuity in the variation of the phys. properties of compds. of the compn. $(C_6H_5)_n$ and $(C_6H_5)_nS$ are removed by assuming that raw rubber is a complex system of mols. of various degrees of polymerization (cf. Bary, C. A. 21, 670) and that the coeff. of polymerization n is only a mean value. Two types of polymers may be present, α and β , with widely different n values and transformable into each other by changes of temp., elongation, soln., light, etc. Since the higher the temp. the lower the mean degree of polymerization, vulcanization at low temps. requires less S than vulcanization at higher temps., e. g., 140-5°. Satn. of the available double bonds at vulcanizing temps. does not assure the formation of a rubber resistant to heat or to repeated mech. work, and if the temp. is raised above that of vulcanization, renewed depolymerization occurs and the rubber is again uncured. The expts. of Bacon do not take into account the more recent theories involving colloidal properties, though there is no evidence offered which is at variance with any of the latter. C. C. DAVIS

Modern developments in the rubber testing laboratory. T. L. GARNER. *India Rubber J.* 76, 705-9(1928).—Various types of app. are described and illustrated. C. C. DAVIS

Determination of the specific gravity of rubber mixtures. ST. REINER. *Gummi-Ztg.* 43, 371(1928).—Comments on a paper by Stoll (cf. C. A. 23, 544). The methods suggested by R. are claimed to be convenient and satisfactory. Reply. L. STOLL. *Ibid.* 371. C. C. DAVIS

Determination of the specific gravity of rubber mixtures. P. ZILCHERT. *Gummi-Ztg.* 43, 310, 312(1928); cf. Stoll, C. A. 23, 544.—A convenient method for detg. the d. of small samples (e. g., 0.05-0.10 g.) is the use of a series of I-KI solns. of different concns., i. e., of different d., in which the samples can be immersed. For larger samples (e. g., 3-5 g.) the well-known method of using a Jolly balance is recommended. C. C. DAVIS

Critical comments concerning carbon black for rubber mixtures. F. KIRCHHOFF. *Gummi-Ztg.* 43, 309-19(1928).—A discussion of the chem. compn. of com. blacks, in which recent papers of Esch (cf. C. A. 23, 306) and Beaver and Keller (cf. C. A. 22, 3802) are discussed critically. C. C. DAVIS

Absorption of the vapors of liquids by rubber. WLČECK. *Gummi-Ztg.* 43, 310(1928).—In view of recently published expts. of Reiner (cf. C. A. 23, 544) brief reference to similar but unpublished expts. of W. is made. In an atm. satd. with benzene or with benzine, rubber absorbed up to about 300 and 150%, resp., of its own wt. at ordinary temp. C. C. DAVIS

Absorption of the vapors of liquids by rubber. ST. REINER. *Gummi-Ztg.* 43, 370(1928).—Comments on a paper by Wlček (cf. preceding abstr.). C. C. DAVIS

Vulcanization of latex. PHILIP SCHIDROWITZ. *Rubber Age* (N. Y.) 24, 263-4(1928).—The process embodied in a recent patent of S. (cf. U. S. Patent 1,682,857, C. A. 22, 4008) is described in detail, with examples of its application. C. C. D.

Method of chemical analysis of rubber. MARJA SAGAJLO. *Przemysł Chem.* 11, 331-42(1927).—These methods are essentially similar to earlier published methods. Cf. Collier and Boggs, C. A. 18, 1763. A. C. Z.

The effect of the silent electric discharge on rubber and decalin. GUIDO FROMANDI. *Kolloidchem. Beihefte*, 27, 189-222(1928).—Theoretical considerations of the effect of the silent elec. discharge on liquid and solid substances and the methods of producing such discharges are first described. Decalin (decahydronaphthalene) was used as the solvent for rubber because it is free from O, which would otherwise be set free by the discharge in a very reactive form, because it is non-reactive to H, and because it has a low vapor pressure. The work includes a study of the effect of silent elec. discharges on decalin, natural rubber and synthetic rubber. The action of the discharge on decalin is manifest by a far-reaching structural change, which is accompanied by sp. chem. reactions dependent upon the gas to which the liquid is exposed during the discharge. The primary effect is a splitting off of H and the secondary effect a polymerization of the unsatd. mols. In an atm. of O the reaction result in the formation ozonides, while in an atm. of N the introduction of N in the decalin mol. is induced. Natural rubber dissolved in decalin undergoes an isomerization under the influence of the discharge; and the I no., viscosity, softening point, and mol. wt. decrease until a powdery material results which has been termed cyclorubber because of its inactivity. Synthetic isoprene rubber, which because of its I no. might be termed cyclorubber, reacted similarly with the exception that the mol. wt. increased at first. It is probable that synthetic rubber could be transformed in this manner to approx. natural rubber in phys. and chem. reactions. The effects of the silent elec. discharge on decalin cannot be explained on the basis of ultra-violet light because of the difference in wave lengths and characteristics of the two discharges. L. F. MAREK

Cream from latex. II. Rubber prepared from washed cream. O. DE VRIES, R. RIEBL and N. BEUMÉE-NIEUWLAND. *Arch. Rubbercultuur* 12, 559-71(1928). (In briefer form in English 572-5).—Earlier expts. on the prepn. of centrifuged cream were continued on a larger scale by dilg. the cream again with water contg. NH_3 , and repeating the centrifuging process, dilg. the cream each time. In this way, primary, secondary and tertiary creams were obtained, from each of which the rubber was coagulated with HCO_2H and converted into crepe. The rubber from the original latex was light yellow; that from the primary and from the secondary latex was whitish; that from the tertiary cream was yellow; and that from underlatex was brown. All these rubbers were sticky, indicating that removal of sol. substances tends toward stickiness. The proportion of non-rubber substances in the cream decreased with each successive washing, while that in the underlatex increased, though these changes were not so great as was to be expected. After vulcanization the tensile strength of rubber from cream is lower than that of rubber from the original latex. The rate of vulcanization diminishes with each successive washing. Rubber from rewashed cream is plastic and has a low viscosity. Underlatex from washed cream yields a plastic rubber with a relatively low viscosity, and (when vulcanized) an abnormally high slope of its compression curve. The NH_3 may play a part in these effects (cf. *Arch. Rubbercultuur* 9, 392(1925); 11, 343(1927)). On keeping for a year or more the viscosity of the rubber from cream diminishes, while the d_{30} value does not change, with no evidence of progressive tackiness or resinification. On keeping, the abnormally high slope of the compression curve (*loc. cit.*) for rubber from secondary and tertiary cream disappears, the high viscosity of the primary underlatex also disappears, and d_{30} remain fairly const. Rubber from secondary and from tertiary underlatex becomes weaker on keeping. Centrifuging does not give a particularly uniform rubber (cf. Blommendaal and van Harpen, *C. A.* 22, 509), since a considerable quantity of serum substances remains in the cream the removal of which increases the time of cure by 20%. Non-rubber substances absorbed and held by the rubber may influence the rate of vulcanization. C. C. D.

Accelerator classification with regard to aging properties. ANON. *India Rubber J.* 75, 585-6(1928).—A criticism of the classification of accelerators given by Dinsmore and Vogt (cf. *C. A.* 22, 4273, 4876). In testing the antioxidant power of accelerators, it is misleading to use the same type of mixt. because certain ingredients have a favorable action on some accelerators and an unfavorable action on others. It is claimed that with accelerators present, accelerated aging tests (air or O) often fail to duplicate the results of natural aging. C. C. DAVIS

Accelerators as antioxidants. R. P. DINSMORE and W. W. VOGT. *India Rubber J.* 75, 824(1928); cf. preceding abstr.—A reply. A single type formula is justifiable in that there are no ingredients known which influence differently the antioxidant properties of accelerators. Good aging of vulcanizates is often attributed to a beneficial action of the accelerator used, whereas the natural antioxidants of the rubber are responsible. Reply. ANON. *Ibid* 824.—Cases are cited to show that certain well-known ingredients influence the aging of vulcanizates when used in conjunction with certain accelerators.

Many accelerators give resistance to aging in addn. to that of the natural antioxidants.

C. C. DAVIS

Dispersoidological investigations. XXIII. The dispersoidology of rubber. I. P. P. VON WEIMARN *et al.* *Repts. Imp. Ind. Res. Inst. Osaka, Japan* 9, 9-50(1928); cf. *C. A.* 22, 4029.—The dispersoidological investigation of natural rubber was undertaken as a preliminary to a study of the conditions under which other substances may be obtained in the rubber-like state. *Hevea* latex and Vultex (preserved with NH_3) contain particles of many shapes, including spheres, egg- and pear-shapes and particles with tails. Particles with such shapes may be found in any emulsion whose drops of disperse phase are coated with a plastic membrane. The original form of *Hevea* latex particles is spherical; the secondary shapes are the result of deformation and flowing together during movement in plants. Spherical particles were observed in latex with diams. from several tenths of μ to 3.5 μ . The longest particle with a tail was 6.7 μ . The particles are believed to consist of "liquid-gelatinous isospherulites" of latex, surrounded by a transitory envelope composed chiefly of proteins with an admixt. of resins. The existence of an intermediate layer of solid polymer of rubber as postulated by Freundlich and Hauser is questioned. Latex particles can be caused to flow together by squeezing them or by adding satd. aq. LiI soln., which is a powerful dispergator for proteins. No evidence of microscopical inhomogeneity of the contents of *Hevea* latex particles was obtained, though the presence of the Tyndall effects proves them to be ultramicroscopically disperse. During vulcanization, all of the rubber contents of latex particles become vulcanized, but though the viscosity of the contents of the particles becomes very great, the particles are still capable of flowing together under pressure. Latex and Vultex can be coagulated by mixing with equal vols. of very concd. aq. solns. of LiI, LiCNS, $\text{Ca}(\text{CNS})_2$, CaCl_2 , $\text{Ca}(\text{NO}_3)_2$ or polyphenols and then washing the coagula very thoroughly in water. The consistency of the dispersion during gelatinization passes through 5 stages, characterized, resp., by very high viscosity, gruel-like consistency, sticky elastic threads, plasticity and high elasticity. A coagulum may possess different consistencies in its different parts. Rods of latex coagulated in test tubes can be stretched to more than double their length without breaking and exude a turbid serum contg. uncoagulated particles. The stretched rods possess a silky gloss, because of their fibrous structure. On releasing they retain a residual elongation which decreases slowly with time. Fresh jellies are distinctly vectorial in properties and may be torn apart easily in the longitudinal direction. Rods of Vultex made in the same way are more easily torn to pieces, do not stretch so far, but require more force for stretching them, contain more uncoagulated particles, and are much more porous in structure. Microscopical and ultramicroscopical study of latex in each of its 5 stages of consistency show that in the viscous stage the latex particles are only beginning to flow together, most of them being still free and in Brownian movement. In the gruel-like stage the particles are clotted together but still retain their individuality. In the stage of sticky threads the rubber contents of contiguous particles have flowed together, so that on deforming the mass, long threads of united particles are produced. In the plastic stage the dispersion medium is rubber in which are dispersed pieces of the non-rubber substances formerly constituting the particle envelopes. In the highly elastic stage the rubber mass has a fibril structure resulting from strains in the films. The changes in consistency of rubber, like those in natural silk, are typical of "coagulation or change in consistency by movement." The only essential difference between the gelatinization of Vultex and that of latex is that the flowing together of the contents of the particles is slower in the Vultex. The structures possible in latex or Vultex jellies are exceedingly numerous, and vary greatly with the age of the jellies and their mech. treatment. Fresh jellies are poly-disperse, micro- and ultramicro-cellular (membranous) jellies. Old jellies possess a fibril structure which may be latent, *i. e.*, the jelly may seem to be ultramicroscopically homogeneous. Lamellar structure is also possible in latex and Vultex jellies. The cause of the high elastic properties of rubber lies only in the inner rubber contents of the latex particles, not in the proteins and resins forming the envelopes of the particles. It is assumed that rubber is a mixt. of liquid and solid polymers, the former changing very slowly into the latter, and that the mol. of rubber has a spiral structure.

F. L. BROWNE

The Research Association of British Rubber Manufacturers. ANON. *Rubber Age* (London) 9, 414-20(1929).—An illustrated description of the new laboratories.

C. C. DAVIS

Dispersoidological investigations on latex. PHILIP SCHIDROWITZ. *India Rubber J.* 76, 875(1928).—A review of a paper by von Weimarn (cf. *Bull. Chem. Soc. Japan* 1928, 157; *Repts. Imp. Ind. Res. Inst.* 9, No. 5(1928)).

C. C. DAVIS

Making rubber goods of latex by electrodeposition. PAUL KLEIN. *India Rubber J.* 76, 879-81(1928).—A description of early expts. and present developments in the

Klein process of electrodeposition of rubber (cf. *C. A.* 19, 3037; K. and Szegvari, *C. A.* 21, 512, 2576, 2820; K. and Healey, *C. A.* 22, 4007; Dunlop Rubber Co., K. and Healey, *C. A.* 22, 4877). Methods involving deposition directly on a metallic surface are preferable to those involving porous diaphragms. Cataphoresis takes place independent of the current strength, whereas electrolytic deposition can take place only above a certain decompn. tension. Therefore, below this tension homogeneous deposits are formed directly on metal with no evolution of gas. This method requires low currents and therefore is slow. Deposition also takes place above the decompn. tension, so that addn. to the latex of certain electrolytes having a lower decompn. tension than water, *i. e.*, OH ions, and which give solid anodic products, can be used. Sulfides and thiosulfates are particularly effective, since S is liberated and forms a homogeneous mixt. with the rubber. The generation of gas at the anode is caused chiefly by OH ions in the serum, and so if these are diminished and an anode which ionizes continuously and combines with the OH ions is used, generation of gas is avoided. The quantity of rubber deposited is a function of the c. d. The following equations (where V is the velocity of migration, H the potential applied, D the dielec. const. of the bath, Σ the absorption potential of the globuloids, μ the internal friction of the liquid, i the current strength and χ the cond. of the liquid): $V = HD\Sigma/(4\pi\mu)$; $H = Ai/\chi$, and $V = (AiD\Sigma)/(4\pi\mu\chi)$ show that the velocity of migration is inversely proportional to the cond. of the bath. These equations were not strictly true in actual expts. but the thickness of the deposit decreased with increase of cond. The concn. of bath is of industrial importance, a change of concn. between 20 and 30% making little difference, whereas with a concn. below 10%, the quantity of rubber deposited varies greatly with slight changes of concn. Deposition must be at a const. rate to avoid continual change of time, c. d. and cond. Methods have been developed for keeping the concn. of the mixt. practically const., a diaphragm between the latex and cathode with the latex compd. inside the diaphragm and contg. the anode causing migration and deposition of rubber on the anode and electroosmotic flow (the inverse of cataphoresis) through the diaphragm so that the serum passed to the cathode. Since alky., concn. and cond. remain const., the rate of deposition is also const. for a given current. The process has been made very economical, 0.2 kw.-hr. being sufficient for the deposition of 1 lb. of rubber mixt., even with cathode diaphragms. The quality of the vulcanized products is superior to that of the corresponding mixts. made by standard methods of milling. The process offers new uses for rubber, particularly in the coating of metals with soft or hard rubber.

C. C. DAVIS

Stress-strain curves of raw rubber-carbon black mixtures at low temperatures. M. KRÖGER AND WAN-NIEN YAO. Univ. Leipzig. *Gummi-Ztg.* 43, 649(1928).—In expts. on the effect of chilling (-20° to -65°) on the stress-strain curves of raw rubber it was found that the stress-strain curves at low temps. conform closely to the stress-strain curves of the vulcanized rubber at normal temps. Further expts. now show that the incorporation of gas black into raw rubber changes the stress-strain curves at these low temps. in much the same way that it changes the stress-strain curves of the vulcanized rubber at normal temps. With Congo, Para and sheet rubber, 10 parts of gas black per 30 parts of rubber were added, and with crepe, 10 parts per 20 parts of rubber. The optimum absorption of energy was at -25° , for though at lower temps. higher stresses were obtained, the disproportionately low elongations made the total energy less. The optimum is then, in comparison with that of pure rubber, displaced toward a higher temp., and is also increased in magnitude by the addn. of the gas black. Further details are published elsewhere (cf. *Z. Elektrochem.* 34, 725(1928)). C. C. D.

Blacks for rubber mixtures. WERNER ESCH. *Gummi-Ztg.* 43, 421-2(1928); cf. *C. A.* 23, 306.—A discussion of properties of different types of C black, with particular comments on papers by Kirchhof (cf. *C. A.* 23, 731) and by Johnson (cf. *C. A.* 22, 4273).

C. C. DAVIS

Reply to the "corrections" of Dr. W. Esch, Hamburg. F. KIRCHHOF. *Gummi-Ztg.* 43, 422-3(1928).—A further polemical discussion of the properties of blacks.

C. C. DAVIS

Determination of sulfur in rubber by the perchloric acid method. EDWARD WOLESENSKY. Bur. Standards, Washington. *Ind. Eng. Chem.* 20, 1234-8(1928).—In a search for a rapid and accurate method for detg. S in rubber, it was found that oxidation by means of Na_2O_2 in a Parr bomb is unsatisfactory when the S content is low, because the samples which can be used are too small for accurate results, and with larger samples oxidation is incomplete. The use of a mixt. of HNO_3 and HClO_4 as described by Kahane (*C. A.* 21, 2817) is also unsatisfactory, but with certain modifications his method may give very good results, and if fusions are unnecessary, it will save time and labor. The chief modifications recommended are the use of more dil. HNO_3 ,

(equal vols. of concd. acid and water), allowing the rubber to dissolve completely on the steam bath before heating more strongly, then heating to gentle boiling until oxidation is complete, and finally destroying the residual HNO_3 by HCl . The use of a larger flask (500–800 cc.) is also recommended, and suggestions are made for the adaptation of this method to the analysis of rubber mixts. which contain Ba, Pb, etc. It is recognized that this method has its limitations and that there are cases where it is inapplicable, but in the majority of cases it should be useful.

C. C. DAVIS

Importance of temperature and humidity control in rubber testing. I. Stress-strain and tensile properties. J. E. PARTENHEIMER, *et al.* *Ind. Eng. Chem.* **20**, 1245–73(1928); *Rubber Chemistry and Technology* **1**, 515–94(1928); cf. *C. A.* **22**, 511.—A report of the Phys. Testing Com. of the Rubber Division of the Am. Chem. Soc. An extensive investigation proves that temp. variations which occur from day to day in an uncontrolled lab. may effect the phys. properties of vulcanized rubber as much as 25–45% in the time of cure, while relative humidity affects the properties relatively little. Furthermore variations in the abs. humidity where the uncured rubber is stored between mixing and curing may affect the tensile strength and modulus as much as does the temp. after curing. Therefore, tests without control of temp. and humidity may be highly erroneous and misleading. The investigation leads to definite recommendations. Uncured rubber mixts. should be conditioned for not less than 24 nor more than 28 hrs. at an abs. humidity of 5.24 grains of water per cu. ft. of dry air (0.012 g. of water per l.), and cured mixts. should before testing be conditioned for not less than 24 hrs. at $80^\circ \pm 2^\circ \text{F.}$ and $45 \pm 3\%$ relative humidity. The testing room should be maintained at $82^\circ \pm 2^\circ \text{F.}$ The time between removing samples from the conditioning cabinets and curing or testing should be not over 2 hrs. If uncured mixts. cannot be conditioned at 82°F. , the relative humidity should be that corresponding to the temp. used, which gives an abs. humidity equal to that obtained under the former conditions, *viz.*, 5.24 grains of water per cu. ft. of dry air. It is not necessary to control the humidity of the testing room, a small cabinet humidified with the proper satd. salt soln. or H_2SO_4 soln. being sufficient. A study of the effect of variations of relative humidity before mixing showed negligible differences in stress-strain and tensile properties, so that it is unnecessary to use more than ordinary care in storing rubber and compounding ingredients. The methods used throughout the investigations are described in detail and the results are recorded in tables and graphs. Control of temp. and humidity are not the only variables in testing rubber, and only when all variables are brought under control will the results of various investigators be strictly comparable.

C. C. DAVIS

Inaccuracies in determination of acidity of raw rubber by water extraction. A. D. CUMMINGS and H. E. SIMMONS. Univ. of Akron. *Ind. Eng. Chem.* **20**, 1213–4(1928).—Expts. on the detn. of water-sol. acids in raw rubber by direct extn. with hot water showed that high and erratic values are obtained, probably on account of *hydrolysis of the esters* present. An increase in the acid no. also takes place if the acetone ext. is boiled with water. In the hot water extn. of rubber, the extent of the ester hydrolysis depends upon the time and temp. of extn., extensive hydrolysis occurring only toward the b. p., which readily accounts for the erratic results of direct extn. where there is uneven heating. To avoid fallacious results in detg. water-sol. acids in rubber ext. first with acetone, and then digest this ext. with water on a boiling-water bath until there is no increase in acidity of the water ext. This is a part of the procedure of van Rossem and Dekker (cf. *C. A.* **21**, 195).

C. C. DAVIS

Normal aging (of rubber). PHILIP SCHIDROWITZ. *India Rubber J.* **76**, 765–6(1928).—A review and discussion of a paper by McKee and Depew (cf. *C. A.* **22**, 2490).

C. C. DAVIS

Reinforcement of rubber by fillers. PHILIP SCHIDROWITZ. *India Rubber J.* **76**, 1071(1928).—A crit. review and discussion of a paper by Blake (cf. *C. A.* **22**, 4876).

C. C. DAVIS

Rubber thread and tape manufacture. A. E. PENFOLD. *India Rubber J.* **76**, 1035–7, 1075–6(1928).—A description of present developments, including the raw materials, methods of compounding, equipment and technic.

C. C. DAVIS

Effect of repeated reclaiming of rubber. GEORGE W. MILLER. Firestone Tire & Rubber Co., Akron. *Ind. Eng. Chem.* **20**, 1165–9(1928).—In view of the increasing importance of the problem whether vulcanized rubber can be reclaimed repeatedly without the quality of the successive reclaims becoming poorer and poorer, a representative whole tire reclaim was cured, was then reclaimed by the NaOH process and the cycle repeated 3 times more. The quality of each new reclaim was detd. by tests, before curing, of the plasticity, acetone and CHCl_3 exts., free and combined S and, after curing, of the tensile strength, ultimate elongation, modulus and aging. Repeated

reclaiming resulted in a decrease in the CHCl_3 ext., plasticity and ultimate elongation and an increase in the acetone ext., combined S and modulus, while the tensile strength remained practically the same. When incorporated in a tire tread mixt. of relatively poor quality, the modulus increased and the elongation and tensile strength diminished with successive reclamations, while by heating in air at 70° there was little difference in the aging properties of the tread mixts. contg. the successive reclaims. The results show in general that when vulcanized rubber is repeatedly reclaimed and recured, its phys. properties become progressively poorer.

C. C. DAVIS

Some observations with ultra-accelerators. A. D. CUMMINGS and H. E. SIMMONS. Univ. of Akron. *Ind. Eng. Chem.* 20, 1173-6(1928).—Several thiuramdisulfides, one of them not previously described, were prepd. and their behavior as accelerators was studied with a view to explaining the mechanism of their action and obtaining evidence for or against existing theories of acceleration. The disulfides were prepd. by the method of Braun (cf. *Ber.* 35, 817(1902)). The following data give the thiuramdisulfides prepd. (the 1st one new)—the m. p. found and the m. p. recorded in the literature: *dimethyldiethyl* (I), 72° , —; *tetramethyl* (II), 146° , 146° ; *tetraethyl* (III), $69.5-70^\circ$, 70° ; *dimethyl* (IV), $101.5-102^\circ$, 102° ; *dimethyldiphenyl* (V), 192° , 198° ; *tetramethyl* (VI), $105-6^\circ$, 106° . IV was almost inactive, whereas II was extremely active (cf. Romani, *C. A.* 16, 854; Twiss, Brazier and Thomas, *C. A.* 16, 2043). On the assumption that inactivity and ease of decompn. may be related, IV was heated alone, with S and ZnO, and with S, ZnO and rubber. In all cases H_2S and MeNCS were evolved. Hence the reaction: $\text{IV} \rightarrow 2\text{MeNCS} + \text{H}_2\text{S} + \text{S}$ proceeds so rapidly that there is little opportunity for cyclic changes involving the activation of S before IV is irreversibly decompd. (cf. Twiss and Thomas, *C. A.* 18, 1764). IV decompd. slowly at room temp. and more rapidly on the steam bath. Heated in a rubber-S-ZnO mixt., VI first evolves alk. vapors, followed by H_2S at higher temps., the mechanism of which probably depends upon the explanation of Bedford and Sebrell (*C. A.* 16, 855) and of Bedford and Gray (*C. A.* 17, 2797). Addn. of II and the equiv. proportion of VI + S to a rubber-ZnO mixt. gave vulcanizates of the same degree of cure, indicating that the same active substance is found in each case, probably Zn dimethyldithiocarbamate. COS passed into ice-cold NH_4Et , the product dissolved in water, satd. with the I, and evapd. yielded an oil which after purification decompd. slowly on standing at room temp. with evolution of H_2S and sepn. of S, which were increased by the addn. of HCl. Boiling and neutralization of this acid soln. gave NH_4Et . The decompns. probably involved the reactions: $[\text{Et}_2\text{NC}(\text{O})\text{S}]_2 \rightarrow (\text{Et}_2\text{N})_2\text{CO} + \text{COS} + \text{S}$; $\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$; $(\text{Et}_2\text{N})_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{Et} + \text{CO}_2$. An aq. soln. of the oil gave with $\text{Zn}(\text{OAc})_2$ a ppt. (probably Zn diethylmonothiocarbamate), which had some accelerating power. Comparative tests showed that accelerators derived from an ethylamine are more rapid than the corresponding ones from a methylamine. The dithiocarbamates were more active than the corresponding thiuramdisulfides. The data are recorded in detail, including artificial aging tests.

C. C. DAVIS

Accurate method for comparison of scorching qualities of accelerators. H. R. THIES. Miller Rubber Co., Akron. *Ind. Eng. Chem.* 20, 1223-7(1928).—A discussion of various methods already known for judging the scorching caused by accelerators leads to the conclusion that none is satisfactory and that there is still need for a simple and reliable method. The new method described overcomes to a large extent the shortcomings of previous methods, and is based on the fact that when a rubber-S-accelerator-ZnO mixt. begins to vulcanize its tendency to disperse in gasoline rapidly diminishes. A mixt. is heated for a given time at a definite temp., is then shaken with gasoline under standardized conditions and the obscuring power of the resulting liquid is then measured. An arbitrary point in the degree of obscurity is chosen as the crit. point at which scorching begins. By varying in a systematic way the time, temp. and proportions of S and accelerator and detg. the crit. points at which the soly. of the heated mixts. begin to diminish, it is possible to obtain useful information on the behavior of different accelerators. To obtain an adequate idea of the behavior of an accelerator, crit. point detns. should be made at 2 or 3 temps., one corresponding to the milling temp., another to the warm storing temp. of the mixt. and another at room temp.

C. C. DAVIS

Heat transfer in the vulcanization of rubber. T. K. SHERWOOD. Hood Rubber Co., Watertown, Mass. *Ind. Eng. Chem.* 20, 1181-5(1928).—The paper is based upon exptl. data, the results of which are given graphically. The temp. lag which prevails in the heating of rubber articles causes a marked non-uniformity of cure in the product. The theory of an "unsteady state" of heat flow is discussed and a method of analyzing data on temps. in a rubber article while heated is described. From data on the temps. at different times during the heating and on the relation between the rate of cure and the temp., the method for calcg. the resulting vulcanizing effect at different points in a solid

rubber object is shown. A new "water cure" process for tires is described, a process which is very effective in reducing the non-uniformity of cure resulting from temp. lag, and at the same time reduces appreciably the necessary time of vulcanization. C. C. D.

The rubber industry in 1928. SIDNEY A. BRAZIER. *Ind. Chemist* 5, 8-11(1929). E. H.

The chemistry and synthesis of rubber. A. HOWARD. Dunlop Rubber Co., Australia. *Chem. Eng. Mining Rev.* 21, No. 241, 31-2(1928).—A brief historical review. C. C. DAVIS

The colloid chemistry of rubber. BENTON DALES. *India Rubber World* 79, 53-7(1929).—A review, dealing with various phases of the subject, with numerous references to the literature. C. C. DAVIS

The history of elastic fabrics. JOSEPH ROSSMAN. *India Rubber World* 79, 59-62 (1929).—A description of various types, with a review of patents. C. C. DAVIS

General laboratories of the U. S. Rubber Co. ANON. *India Rubber World* 79, 63-4(1929).—An illustrated description of the new labs. C. C. DAVIS

Rubber. KURT H. MEYER AND H. MARK. *Ber.* 61B, 1939-49(1928).—New and very careful measurements on x-ray diffraction patterns of stretched rubber give, as the dimensions of the unit, a rhombic cell $a = 12.3 \pm 0.1$, $b = 8.3 \pm 0.1$, c (fiber axis) $= 8.1 \pm 0.1$. The space group is V_4 , which specifies 3 two-fold screw axes. It is perfectly clear that the structural mols. form micelles whose form and size may be detd. from the breadths of the x-ray interferences. The av. length of a crystallite is thus 300 to 600 A. U., thickness and breadth 100 to 200 A. U. Since each unit cell contains 8 C_5H_8 groups, the micelle contains 10,000-20,000 unit cells or 80,000-150,000 isoprene groups. In stretched rubber there are long chains contg. 75-150 isoprene groups held together by primary valence forces. These long chains lie parallel to each other along the fiber axis, and the small unit cell represents simply a turn in the screw axis. The olefin character of isoprene accounts for the fact that in unstretched rubber these long chains may contract and spiral, because of the mutual effects of the double bonds. Under these conditions the structure does not permit x-ray diffraction, although the preformed structural units are present. New expts. on the osmotic pressure of dissolved rubber are reported. These results indicate mol. wts. from 150,000 up to nearly 400,000 on account of the very high degree of solvation. Practically all of the benzene or chlorobenzene is bound to the rubber micelles. New expts. are also reported on cold vulcanization with S_2Cl_2 . Rubber shows a close analogy in its reaction to that between ethylene and SCl_2 or S_2Cl_2 to form mustard gas. The compd., $C_{10}H_{16}SCl_2$, is identified. Many of the properties of vulcanized rubber are accounted for in the formation of bridges between double bonds in the same micelle and in the connection between double bonds of different micelles. These new bonds, therefore, decrease the elasticity, and in the limit lead to hard rubber in which the micelles are solidly bound together. G. L. CLARK

Aging of rubber. ALFONS ZELNICEK. *Chem. Obsor* 3, 223-43, 257-63(1928).—A discussion of the causes of aging, aging tests, proposals for storing *in vacuo*, in inert gases, under water and chem. means for the preservation of rubber, with a bibliography. JAROSLAV KUČERA

The aging of rubber under tension. GABRIEL G. BALAZS. *India Rubber & Tire Rev.* 28, No. 10, 20(1928); *Gummi-Ztg.* 43, 708, 710.—Mixts. with and without antioxidants were aged under different conditions, while stretched and while not stretched, to det. the influence of the various factors involved on the rate of deterioration. The results are given in tabular form and admit of certain conclusions. In all cases the greatest deterioration occurred with elongations of 0-50%. At 50-100% elongation the aging was the same as with the corresponding unstretched samples. Because of the permanent elongation the tension diminished during the aging periods. The rate of deterioration was not proportional to the initial elongation. The relative rates of deterioration in the hot air oven and in the O-bomb depend upon the presence of antioxidants, the latter rendering the samples relatively more resistant in the O-bomb. The acetone ext., a measure of the chem. changes during aging, increased with the time of aging. It was not proportional to the initial elongation. Because of fatigue phenomena in the stretched samples, the phys. properties were influenced to a greater extent than is accountable by O absorption alone. A decrease in wt. in the hot air oven indicates that either free S or antioxidant, or both, are volatilized. No definite relations could be found between increase or decrease in wt. and the % elongation. In every case, however, stretching resulted in a slight decrease in wt. The permanent elongation was smaller after aging in the O-bomb than after aging in the hot air oven, so that the samples in the O-bomb were under greater tension than were the corresponding samples in the hot air oven. C. C. DAVIS

Technical application of antioxidants. E. R. BRIDGWATER. *India Rubber World* 79, 61-2(1929).—A review and discussion, dealing with the characteristics of antioxidants, *reversion phenomena*, *anti-softeners*, *cracking under tension*, *sun-checking* and *methods of testing the aging of rubber mixts.* The view is taken that the term "antioxidant" should be broadened to include all substances which retard the deterioration of rubber, whether this deterioration results from oxidation or from other causes. The tendency toward reversion in overcured mixts. is considerably diminished by anti-softeners, for the continued stiffening effect induced by the latter counteracts the softening which sets in after the free S is exhausted. Some compds., e. g., phenyl- α - and phenyl- β -naphthylamine, are very effective in preventing cracking under tension. Used in conjunction with an anti-softener, they are therefore of great value in the numerous types of rubber products which deteriorate on this account. Emphasis is laid on the importance of testing rubber products by some method more closely simulating the performance of the products than the usual methods. These performance tests should be carried out before and after artificial aging in air or in O. C. C. DAVIS

The isomerization of rubber to cyclorubber under the influence of high-tension alternating currents. GUIDO FROMANDI. *Kautschuk* 4, 185-9(1928).—Substantially the same as C. A. 23, 1009 only in briefer form, with fewer data. **Correction.** *Ibid* 262.—Addn. to charts explaining the curves. C. C. DAVIS

Determination of the iodine number of raw rubber. ADOLF GORGAS. Lab., Runge-Werke A.-G., Berlin-Spandau. *Kautschuk* 4, 253-4(1928).—If in the Wijs-Kemp method for detg. the I no. of rubber (cf. K., C. A. 21, 1901), the ICI-AcOH soln. is replaced by IBr-AcOH, i. e., by Hanus soln. (cf. Z. *Nahr. Genussm.* 4, 913 (1901)), the reaction at 0° is incomplete. If IBr-AcOH is added to the rubber in CCl₄, coagulation occurs and the reaction is incomplete. At room temp., on the other hand, IBr gives theoretical I values if used under suitable conditions. Replacement of AcOH by CCl₄ is all that is necessary. **Procedure.**—As reagent dissolve 10 g. of IBr in 500 cc. of pure CCl₄. Disperse 0.15 g. of raw rubber in 50 cc. of CCl₄, add 50 cc. of IBr reagent, agitate, let stand 15 min. in darkness, add 30 cc. of 10% KI soln. and 100 cc. of water and titrate with 0.1 N Na₂S₂O₃ until colorless, adding starch near the end point. With vigorous agitation there is no emulsification. From the wt. *s*, the titer *a* of a blank test, the titer *b* of the IBr soln. on titrating back, the *f* of the Na₂S₂O₃ soln. the I no. is calcd. as $(a-b) \times 0.01269 \times f \times 100/s$. Rubber purified from "Revertex" by the method of Pummerer and Pahl (cf. C. A. 22, 885) gave practically the theoretical I no. corresponding to 1 double bond per C₆H₈ unit. C. C. DAVIS

Washing hard rubber dust. MAX RATHKE. *India Rubber World* 79, 69(1929); cf. C. A. 23, 307.—A description, with diagram, of a system devised by R. and now in successful operation in Germany. C. C. DAVIS

Crystallized gutta-percha which is sensitive to light. F. KIRCHHOF. *Kautschuk* 4, 254-5(1928).—Tjipetir gutta-percha contg. 98-9% hydrocarbon was purified by extrn. with cold acetone, soln. in CCl₄, filtration and evapn. of the filtrate. The product was white because of a cryst. structure. Microscopically the crystals were rounded, about 0.5 μ thick and 1-1.5 μ long. When the gutta-percha was heated above 43-4°, they disappeared and on cooling reappeared at 42-38°. Fusion and recrystn. could be repeated indefinitely. Exposed to ultra-violet light, the purified product became brittle and more opaque, even in an atm. of H, the changes probably being the completion of crystn. Exposure of purified gutta-percha in C₆H₆ in an atm. of H gave on evapn. a product which was white, unctuous, and fragile, and which m. at 90° to a limpid oil. On cooling, the latter gave a tough product like the original gutta-percha. Heating thus destroyed the cryst. structure. Gutta-percha in an atm. of H irradiated with ultra-violet lost its turbidity at 39-40°, and this reappeared only at 35°, indicating that the m. p. of the micro-crystals of the irradiated product was definitely lower than that of the original crystals. On evapn. of the C₆H₆ this irradiated product redissolved to a clear soln. in C₆H₆, whereas irradiation of a film with air present gave a product which was partially insol. Exposure to ultra-violet light seemed to increase the ability of the gutta-percha to crystallize. In sunlight and air the chief effect was oxidation. The difference between the behavior of rubber and gutta-percha in ultra-violet light is attributed to the higher state of polymerization of the latter. **Correction.** *Ibid* 272. C. C. DAVIS

Uniting rubber to metal. JOSEPH ROSSMAN. *India Rubber World* 79, 65-8 (1929).—A review and discussion of recent patents, including those for plating with Cu as a binder, the use of bakelite, the manuf. of solid tires, lining metal tanks, metallic fabrics for tires, coating elec. wires and the electrodeposition of rubber. C. C. D.

Fundamental principles of plasticization. JOSEF OBRIST. *Kautschuk* 4, 250-2

(1928); *India Rubber J.* 77, 25-6(1929).—A review and discussion (cf. Manfred and O., *C. A.* 21, 2535).

C. C. DAVIS

Causes of variation in plasticity. CEYLON RUBBER RESEARCH COMM. *India Rubber J.* 77, 32-6(1929).—The present paper deals with tests on crepe rubber 6 months old which had been prepd. by (1) keeping the coagulum in the serum for different periods before rolling; (2) passing the coagulum through the rollers for different nos. of times; (3) adding different proportions of NaHSO_3 to the latex; (4) coagulating latex after different degrees of diln., and (5) passing dry crepe through different types of rolls to convert it into blanket crepe. The results of the expts. indicate that 6 months after prepn.; (1) crepe prepd. by machining the coagulum 3 hrs. after coagulation is approx. 80% more plastic than that prepd. by machining the coagulum 40 hrs. later; (2) crepe is nearly twice as plastic when prepd. from coagulum machined more than 20 times instead of the customary no. of times; (3) crepe is approx. 50% more plastic when prepd. from latex contg. no. NaHSO_3 instead of the proportion officially recommended; (4) crepe is only slightly more plastic when prepd. from very dil. latex than that from concd. latex or from normal latex, and (5) machine-dried crepe may be 50% more plastic than air-dried crepe, and the type of rolls (whether water-cooled or air-cooled) may have an important effect on the plasticity of blanket crepe. The 6 months' storage comprised a short period in Ceylon and 4 months in London, so that the conditions are representative of those normally prevailing in commerce. Both the period during which the coagulum is kept in the serum before rolling, and the proportion of NaHSO_3 may influence the plasticity of com. grades of rubber. Drying crepe in hot air causes considerable increase in plasticity, a fact which is of importance in the prepn. of blanket crepe, and which suggests a reason why smoked sheet is usually more plastic than air-dried sheet.

C. C. DAVIS

Aldehyde derivatives of Schiff's bases as vulcanization accelerators; A-11, A-16, A-19, A-20 and A-50, and the ultra-accelerator Z-88. RUDOLF DITMAR and MANFRED RACHNER. Kautschuklaboratorium, Graz. *Chem.-Ztg.* 52, 935(1928); cf. *C. A.* 22, 4876.—Tabulated data show the soly. of the 6 accelerators in water, benzene, C_6H_6 , CS_2 , CCl_4 and EtOH and their behavior with PbO , ZnO , MgO , and CdO , factice, golden Sb, HgS and 3 "Vulkan" colors (cf. D., *C. A.* 22, 4273).

C. C. DAVIS

The accelerator "Tuads" and its limitations. WERNER ESCH. *Kautschuk* 4, 255-8(1928).—A discussion, with quant. data, of the accelerating properties of "Tuads" (tetramethylthiuramdisulfide), with particular reference to its merits compared with "Thionex" or "Monex" (tetramethylthiurammonosulfide).

C. C. DAVIS

Selenium red, the only red which is stable with all accelerators. RUDOLF DITMAR. Kautschuklaboratorium, Graz. *Gummi-Ztg.* 43, 759-60(1929).—Tests of the value of Se red in rubber mixts. of widely different types showed that it is of almost unlimited application. It can be used whether alone as a pigment or in conjunction with lithopone, ZnO , TiO_2 , etc. It acts as a plasticizing agent, even when only 3% is added to the rubber, and forms a colloidal soln. with the rubber. It is unaffected by any of the com. accelerators or antioxidants or by factice, and can be used in soft or hard rubber mixts. cured with S. It cannot, however, be used when S_2Cl_2 is used as a curative, either as a vapor or in soln. Its coloring power exceeds that of any other inorg. red pigment.

C. C. DAVIS

A further study of the vulcanization of oils. II. P. STAMBERGER. Univ. College, London. *Rec. trav. chim.* 47, 973-6(1928); cf. *C. A.* 22, 506.—Triolein (5 parts) and S (1 part) heated 2 hrs. at 160° yielded a vulcanizate wholly sol. in C_6H_6 . This product digested with acetone (5 parts) for 4 days and the extn. repeated 4 times yielded a residue of increased solidity with diminished soly. in C_6H_6 , and which was slightly elastic. The mol. wts. (dtd. in C_6H_6) of the acetone-sol. and C_6H_6 -sol. products were 1204 and 2040, resp. These products were heated at 180° until gelation occurred, under which conditions the C_6H_6 -sol. substance swelled more and formed an insol. product far sooner than did the acetone-sol. substance. When they were exposed at 40 - 60° to ultra-violet radiation in air and in N, the acetone-sol. substance swelled more than did the C_6H_6 -sol. substance, but the latter formed an insol. product far sooner. When the C_6H_6 -sol. substance was kept under acetone for 3 days, or under water for 8 days, it became elastic and insol. in C_6H_6 . After 3-4 months at room temp. the C_6H_6 -sol. substances became an elastic sticky solid which did not dissolve in cold C_6H_6 but was completely sol. in boiling C_6H_6 , and this latter soln. on evapn. yielded a product sol. in cold C_6H_6 . These results, in conjunction with further swelling phenomena under various conditions, show that the properties of these various substances are altered by soln. It is probable that the low mol. wts. obtained with other gels, such as rubber and cellulose derivs., depend upon a depolymerizing action of the solvents. In the formation of elastic substances from sulfurated triolein, no chem. change takes place, so the change

in behavior toward solvents cannot be explained by the formation of new compds. It is probable that the complete system changes in solvents, mol. polymerization and aggregation taking place.

C. C. DAVIS

Methods of determining abrasion, with particular reference to the relation between road performances and laboratory tests. L. J. LAMBOURN. *Trans. Inst. Rubber Industry* 4, 210-34(1928); *Rubber Chemistry & Technology* 2, 166-92(1929).—The new type of abrasion machine, termed a "controllable slip" abrasion machine (cf. Brit. pat. 282,131), which is described and illustrated, has been so designed that rubber samples are abraded under controlled pressure intensity and slip, which may be regulated before or during the test to meet the conditions to be simulated. In this way the chief factors governing wear, viz., the nature of the surface, the intensity of pressure and the slippage, can be regulated so that each plays the correct relative part, resulting in a close approach to the particular conditions of road wear which it is desired to imitate. The results obtained with the app. indicate that it gives a correct forecast of road performance in 9 out of 10 cases. Expts. show that the work of abrasion is proportional to the magnitude of the slip, so that testing at const. slip is practically the same as testing under const. work. The new app. gives correct results over a greater range of hardness than any previous app. Various facts may be learned or confirmed by the app. Thus it was found that the rate of wear of a tire increased approx. with the square of the slippage, and where one mixt. was better than another at low % slippages, at higher % slippages the order of merit changed so that the mixt. which was inferior at low slippage became more resistant to abrasion when the slippage was high. A relatively hard mixt. is usually best when the speed and therefore the slippage is high, for it consumes less power and does not become so hot. Tests are also described to show the remarkably high rate of wear in summer, the very small wear when rubber is wet and the great effect which the character of the surface, the speed, the acceleration and the construction of an automobile have on the wear of tires. Various other subjects relating to abrasion and lab. and performance tests are discussed. C. C. D.

Patents

Stabilized latex containing blood protein. MORGAN R. DAY (to Rubber Latex Research Corp.). U. S. 1,689,581, Oct. 30.

Softening and preventing aging of rubber. G. FESSEL and TECHNISCHE CHEMIL-KALIEN Co. GRS. Brit. 286,171, Sept. 21, 1927. A softening and "anti-aging" ingredient for use in the manuf. of rubber goods is prep'd. by extg. the phenolic constituents and aromatic bases contained in tar produced by the distn. of coal, lignite, shale or peat, or in distillates from such tars, and subsequently removing any undesirable light oils. "Methylated spirits," MeOH, EtOH, acetone or EtOAc or their mixts. which may be dild. with water are suitable solvents and soda lye and C_2H_5 may also be used in some cases. The oils obtained are preferably heated to 135-50°, allowed to cool and then added to rubber mixings or scrap rubber in the proportion of 5-10%.

Roller apparatus for mixing and sheeting rubber. L. GRAFFE. Brit. 285,712, June 22, 1927.

Rubber-mixing apparatus. FERNLEY H. BANBURY (to Farrel-Birmingham Co.). U. S. 1,689,990, Oct. 30.

Preserving rubber. L. B. SEBRELL (to Goodyear Tire & Rubber Co.). Brit. 286,288, March 3, 1927. The aging qualities of rubber are improved by adding to the mixt. before vulcanization, a reaction product of an aldehyde and an amine (such as the product from aniline and acetaldehyde) which is formed in a cold reaction mixt. and is not an active vulcanization accelerator. Cf. C. A. 22, 3551.

Preserving rubber articles during storage. THOMAS M. RECTOR (to Vitapack Corp.). U. S. 1,688,355, Oct. 23. Inner tubes for tires or other closed rubber articles are filled with N_2 , CO_2 or other inert gas and also surrounded by inert gas within a sealed container which may be made of sheet metal.

Deposition of rubber. SOCIÉTÉ DU CAOUTCHOUC "ANODEX." Fr. 638,504, Nov. 27, 1926. A partition of glass or ceramic material or cloth is placed between the cathode and the support for the electrophoretic deposition of rubber to keep the rubber free from gas bubbles formed at the cathode. Cf. C. A. 22, 3551.

Reinforced hard rubber. WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,689,570, Oct. 30. In forming a material suitable for battery jars, insulation, etc., comminuted hard rubber is admixed with disintegrated partially cured rubber, S. fiber such as reclaimed cotton, and with rubber latex, and the mixt. is dried, molded and vulcanized.

Bonding rubber to metal. HAROLD GRAY (to B. F. Goodrich Co.). U. S. 1,689,628, Oct. 30. A vulcanizable rubber compn. is superposed on steel or other metal with an interposed film comprising S chloride in direct contact with the metal and vulcanizing is effected by heating at a usual vulcanizing temp. Cf. C. A. 22, 3318.

Rubber articles. "COGEDEX" COMPAGNIE GÉNÉRALE D'EXPLOITATION. Fr. 638,304, July 27, 1927. The rubber gum, after incorporation of the S and fillers, is put directly into the mold for vulcanization.

Rubber articles formed by dipping. DUNLOP RUBBER CO., LTD., and D. F. TWISS. Brit. 285,938, Oct. 22, 1926. Before dipping a mold in latex compn. or the like, the mold is first coated with gelatin or the like contg. a coagulant such as Na fluosilicate, HOAc, or a salt of Ca, Mg, Zn or Al. The mold or bath is agitated to make the deposit more uniform.

Molded rubber articles formed by dipping. ANODE RUBBER CO., LTD. Brit. 285,844, Feb. 23, 1927. The mold is heated during the intervals between successive dippings in a dispersion of rubber, and may also be heated during the dippings, *e. g.* by a circulating heating fluid or by elec. current.

Molded articles of cork and rubber composition. RAOUL GRIMOIN-SANSON and HERMAN DANIEL. U. S. 1,688,491, Oct. 23. Tires, tire treads or other molded vulcanized articles are formed of a mixt. comprising rubber, powd. cork, emery and a vulcanizing agent.

Rubber threads, tapes and strips. INDIA RUBBER, GUTTA PERCHA & TELEGRAPH WORKS CO., LTD., and E. J. SMITH (known as E. J. Edgar). Brit. 286,066, Feb. 10, 1927. A sheet of unvulcanized rubber is applied to a supporting surface such as tin-foil to which it will lightly adhere after vulcanization, is vulcanized, cut into threads or strips, and then stripped from the supporting surface. An app. is described.

Plastic moldable composition containing rubber. CARL KULAS. U. S. 1,688,500, Oct. 23. A mixt. of comminuted rubber and dissolved "resol" (an initial condensation product of CH_2O and phenol) is rapidly calendered to expel volatile constituents and render the mass homogeneous, the latter is seasoned at a moderate temp. (suitably about 30-40°) which is maintained const. during the seasoning and the material is dried. It is suitable for *elec. insulation*, etc.

Treating waste rubber. RHEINISCHE GUMMI- UND CELLULOÏD-FABRIK. Fr. 638,396, July 28, 1927. Waste rubber is powdered and added to a non-volatile nitro-cellulose solvent such as triphenolphosphate, palatinol, acetanilide, ethylacetanilide or plastol, which lowers the m. p. of the camphor contained in the rubber, after which the mass is submitted to heat and pressure.

Composition for sealing punctures in pneumatic tires. ERNEST E. BOARD. U. S. 1,690,051, Oct. 30. A mixt. is formed from bran 1, flaxseed meal 1, corn sirup 2 parts, and 2 parts of an anti-freeze soln. contg. CaCl_2 27.5%, and K chromate 1 part, with water to make a pasty compn. suitable for introducing into a tire.

Rubber substitute. LOUIS LAURIN. Fr. 638,559, Dec. 11, 1926. An elastic compd. which may be used for pneumatic tubes, etc., is made from chrome-tanned colloids with which a double sulfate of Al and K, glycerol and, if necessary, formol are combined. In an example 100 parts of gelatin, 5 of $\text{K}_2\text{Cr}_2\text{O}_7$, 2 of the double sulfate, 80 of water, 90 of glycerol and 3 of formol are used.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 286,272, March 2, 1927. Polymerization of hydrocarbons such as isoprene, butadiene and dimethylbutadiene is effected in an aq. colloidal soln. soln. or suspension contg. one or more electrolytes (which may in general be acids, bases or salts, either inorg. or org., with good elec. conductivity), either in the presence of O , ozone or substances which produce them or in an inert atm. such as N or CO_2 ; *e. g.*, dimethylbutadiene is agitated with egg albumin and Na phosphate in water at a temp. of 80°. Numerous other examples are given. Cf. C. A. 22, 4274.

Vulcanizing rubber. CECIL J. T. CROMSHAW and W. J. S. NAUNTON (to British Dyestuffs Corp., Ltd.). U. S. 1,687,861, Oct. 16. Di-xylylguanidine is used as an accelerator.

Vulcanizing rubber. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,688,755, Oct. 23. A vulcanized product of good "age resisting" properties is obtained by heating rubber and S together in the presence of a reaction product of guanidine or a diaryl-substituted guanidine and hydroquinol or other hydroxy deriv. of benzene. U. S. 1,688,756 specifies the use of *p*-dimethylaminophenyl-*p*-phenetidyl guanidine as a vulcanization accelerator. U. S. 1,688,757 specifies the use of *p*-dimethylaminodiphenylguanidine and U. S. 1,688,758 specifies *p*-dimethylaminophenyl-*o*-tolylguanidine.

Treating latex. WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,690,150, Nov. 6. A reaction is effected between ZnO and hemoglobin in soln. in latex to obtain a material which may be subsequently coagulated for various purposes.

Rubber compositions. L. B. SEBRELL (to Goodyear Tire & Rubber Co.). Brit. 287,445, March 19, 1927. Reaction products of crotonaldehyde and amines such as toluidines, xylydines or naphthylamines are used as "antiagers" for rubber.

Rubber composition for sealing containers, etc. ARTHUR BIDDLE (to United Products Corp. of America). U. S. 1,691,460, Nov. 13. A compn. of adhesive properties comprises an aq. dispersion of chicle, a hydrophilic colloid such as casein, an oil solvent for the chicle such as linseed oil, rubber in dispersed phase and an alkali such as NH_3 and borax.

Composition of rubber and fibers. THE DUNLOP RUBBER CO., LTD. Fr. 637,211, July 7, 1927. Objects are made by molding and vulcanizing a material contg. 75% or more of waste tires and tubes, or other waste from the manuf. of tires, and if desired, filling materials. In an example, 29 parts of waste auto covers ground small, 28 of cloth scraps or waste cord, 28 of old rubber tires, 10 of S, 2 of mineral oil, 2 of brown substitution product, and 1 of stearic acid are mixed and vulcanized under pressure.

Deposition of rubber. WM. A. WILLIAMS. Fr. 638,630, June 22, 1927. In the electrophoretic deposition of rubber an exterior source of current is dispensed with by adding to the latex, vulcanized or not, an electrolyte such as NH_4Cl which acts as an auto-excitant, and connecting the electrodes of Zn and C directly outside the electrolyte. If the latex of commerce is used its alky. is first reduced.

Forming rubber tubes from solutions or dispersions. DUNLOP RUBBER CO., LTD., D. F. TWISS AND E. A. MURPHY. Brit. 287,592, Oct. 21, 1926. Mech. features.

Forming tires in metal molds. WALLACE H. CAMPBELL (to Goodyear Tire and Rubber Co.). U. S. 1,691,756, Nov. 13. A tire is supported in a metallic mold blank in spaced relation to the blank, the intervening space is packed with a casein compn. and the materials are subjected to heat and pressure to harden the compn. and form a tread mold for tire manuf.

Molded rubber articles formed by dipping. DUNLOP RUBBER CO., LTD., G. W. TROBRIDGE AND E. A. MURPHY. Brit. 287,946, Oct. 20, 1926. The mold is treated, on the side which is to take the deposit, with materials which facilitate the agglomeration of the rubber from latex or other aq. dispersions, *e. g.*, with CaCl_2 , with or without fillers, S, accelerators, etc. The pressure on the inside of the mold may be reduced or that on the outside increased, or the mold may be partially glazed so that a thinner deposit is formed on the glazed than on the unglazed portions.

Utilizing waste rubber for belting, etc. I. BONTEMS. Brit. 286,652, March 7, 1927. Articles such as driving, conveyor or elevator belts are made from old tire casings (from which the beads or flanges are removed) which are partly devulcanized and then revulcanized in stretched-out position.

Composition for filling shoe bottoms. H. BROOMFIELD AND SHOE INVENTIONS, LTD. Brit. 287,206, Dec. 7, 1926. Various materials are used together, of which an example comprises ground vulcanized rubber 56, leather or cork dust 16, cotton, leather or wool fiber 2, a soln. of bitumen in light hydrocarbon with or without collodion 24, raw rubber soln. 48, S 2 and accelerator 1 part.

Molding ebonite. A. FRASER AND RISSIK, FRASER & CO., LTD. Brit. 286,915, Nov. 2, 1926. In subjecting ebonite dust to pressure and heat, molds are used, the inner surfaces of which are composed of materials such as Sn, brass, duralumin or other Al alloy, rustless steel contg. no Ni or an alloy such as described in Brit. 250,721 (C. A. 21, 1247), to which the ebonite dust does not stick and with which it does not react. Cf. C. A. 22, 2082.

Molded ebonite articles. HAROLD GRAY (to B. F. Goodrich Co.). U. S. 1,691,347, Nov. 13. Rubber is mixed with a vulcanizing agent such as S and accelerator and with sufficient clay, whiting, C or other suitable pigment to stiffen the compn. after momentary vulcanization, the material is partially vulcanized in a mold, then removed from the mold and subjected to further vulcanization.

Vulcanization of rubber joined to leather. LÉON B. CONANT. Fr. 637,487, July 12, 1927. See Brit. 275,194 (C. A. 22, 2292).

Vulcanized rubber. BRITISH DYE STUFFS CORP., LTD., CECIL J. T. CRONSHAW AND WM. J. S. NAUNTON. Fr. 637,849, July 18, 1927. A material giving good aging properties to rubber is produced by condensing equal parts of α - and β -naphthylamine with AcH in the presence of an acid. An example of a good aging rubber is 45 parts smoked sheets, 30 floating reclaim, 3 mineral rubber, 10 ZnO, 10 gas black, 2 S, 0.3 diphenylguanidine, and 1.2 of the above described compd., vulcanized for 45 min. at 141° .

Treating rubber latex. J. MCGAVACK and R. A. SHIVE (to Naugatuck Chemical Co.). Brit. 288,268, April 8, 1927. Latex having a p_H of 4.5 to 7 is stabilized by sulfonic alkyl aryl reaction products such as the product obtained in the presence of H_2SO_4 or chlorosulfonic acid from cinnamic acid and $BuOH$, or *p*-cresol and oleic acid, or anthracene or naphthalene and $PrOH$ or the like. "Twitchell compds." may be used. Details are given, and the product is stated to dry more rapidly than alk. latex and to be more rubbery and more plastic on the mill.

Preserving latex. I. G. FARBENIND. A.-G. Brit. 289,022, April 20, 1927. Premature coagulation of latex is prevented by addn. of water-sol. neutral or alk. salts of ester acids such as Na dicresylphosphate, K methylsulfate or NH_4 diphenylphosphate. Other preservatives such as NH_3 , amines and alcs. also may be added. Cf. C. A. 22, 1705.

Spray-drying latex. J. E. NYROP. Brit. 289,583, Feb. 15, 1927. Latex is sprayed into a heated gaseous medium by app. such as that described in Brit. 259,922 and anti-coagulating or anti-agglutinating agents such as soap are simultaneously sprayed without being previously mixed with the latex. Softeners, fillers, vulcanizing agents, etc., may also be added by spraying.

Rendering rubber resistant to aging. ALBERT M. CLIFFORD (to Goodyear Tire & Rubber Co.). U. S. 1,694,529, Dec. 11. Rubber is incorporated with a small proportion (suitably about 1-5%) of β,β -dinaphthylamine or other suitable compd. of the general formula $RR'NH$, in which R and R' are similar naphthylene radicals.

Ornamenting sheet rubber with a printing apparatus. IOCO RUBBER & WATER-PROOFING CO., LTD., A. RYAN and J. KIRKWOOD. Brit. 288,411, Feb. 21, 1927. An unvulcanized rubber sheet is backed with a glazed or faced sheet and treated in a printing app. of the calico-printing type and then passed over steam-heated drying plates. This treatment is suitable for material used for making hot-water bottles or the like.

Thin-walled rubber articles. I. DOROGI, L. DOROGI and DOROGI ES TARSA GUM-MIGYAR R.-T. Brit. 288,541, April 11, 1927. The extensibility of dolls or other toys or thin-walled rubber articles is reduced by applying to them a flexible lacquer-like coating (either on the exterior or interior of the articles) preferably contg. a cellulose deriv. which reduces the stretching capacity by at least half. Various details are described.

Puncture-filling composition. B. G. HARRINGTON and R. S. MASON. Brit. 288,917, Nov. 3, 1927. Finely powd. silica 40, alumina 40, mica 10 and soapstone 10% are uniformly mixed with water and evapd. crushed and sifted. Coarse mica, ochre or "gilt dust" may be added.

Rubber composition for sealing joints in can ends, etc. AMERICAN CAN CO. Brit. 289,270, May 28, 1927. Latex is mixed with NH_4 alginate or other suitable "alginic material" and with a "body material" such as calcined Al_2O_3 . Other substances such as sapond. beeswax and NH_3 may also be added.

Liners for use between rubberized fabrics. L. B. SEBRELL (to Goodyear Tire & Rubber Co.). Brit. 288,244, April 6, 1927. Material suitable for use between freshly prepd. rubber coated fabric such as that used for making pneumatic tires consists of fabric coated with nitrocellulose compn. contg. a softening agent such as diethyl phthalate, dibutyl phthalate, diamyl phthalate, tricresyl phosphate or castor oil. The softening agent may be applied to the fabric after the nitrocellulose coating is applied by spraying or dipping.

Preserving the interior surfaces of air bags formed of rubber. STEWART S. KURTZ JR. (to Goodyear Tire & Rubber Co.). U. S. 1,694,879, Dec. 11. A soln. contg. glycerol and a drying oil such as rapeseed or linseed oil is introduced into the interior of bags such as those used in vulcanizing pneumatic tires.

Rubber sheet material. H. BROOMFIELD. Brit. 288,354, Dec. 7, 1926. A sheet material suitable for use in the manuf. of footwear is formed of raw rubber, fillers such as ground vulcanized rubber, lithopone, ZnO , vulcanizing agents and fibers, with a cell-producing agent such as water or $(NH_4)_2CO_3$, without use of naphtha or other softening agent which would cause rupture of the cells. A compn. is specified which may be vulcanized at atm. pressure at a temp. of 90-120°. Various details and modifications are described.

Recovery of used rubber. MAURICE DIT RENÉ GATTEFOSSÉ and SOC. FRANÇAISE DE PRODUITS AROMATIQUES (Anciens établissements Gattefossé). Fr. 636,641, Oct. 20, 1926. Used rubber is boiled with an ester such as an acetate, butyrate, or formate of an alc. such as cyclohexanol, or an ether such as benzyloxy-amy- or -butylcineole, and filtered. The ether is recovered by washing with an alc. or other solvent in which the ether is sol. but not the rubber.

Reclaiming rubber. JOHANN TENGLER. Can. 284,014, Oct. 16, 1928. Pulverized old rubber is mixed with hydrogenated hydrocarbons, e. g., hydronaphthalene, and is subjected to pressure and heat, whereby the H in the hydronaphthalene com-

binies with the S in the vulcanized rubber deposit and is removed as H_2S . Further hydrocarbon is added, *e. g.*, benzine and high pressure and heat are applied and the complete soln. of the mass is obtained. The naphthalene formed from the hydrogenated naphthalene is removed by freezing out. Vulcanization is then effected with natural S by subjecting the mass for a long time to high pressure and heat, whereby hardening of the mass occurs. The mass recovered is suitable as a binding medium for colors, varnishes, cements, etc.

Vulcanizing rubber latex. I. G. FARBENIND. A.-G. Brit. 288,206, April 4, 1927. Latex is vulcanized by successive treatment with SO_2 and H_2S (coagulation being prevented by a medium such as a condensation product from $C_{10}H_8$, CH_2O and H_2SO_4 or sulfonic acids of alkylated naphthalenes or sulfonation products of oils, naphthenic or fatty acids or the like).

Vulcanizing rubber. RUBBER SERVICE LABORATORIES CO. Brit. 286,749, Oct. 6, 1926. Accelerators are produced by combining mercaptans or mercapto compds. with org. bases other than guanidines, *e. g.*, with aldehyde-ammonia reaction products such as $(CH_2)_6N_4$, which gives a resinous product when heated with mercaptobenzothiazole. Biguanide, guanyl ureas, isoureas, thioureas, and isothioureas may be used, and various examples are given. Cf. C. A. 23, 310.

Vulcanizing rubber. RUBBER SERVICE LABORATORIES CO. Brit. 287,001, Oct. 6, 1926. Vulcanization accelerators are produced by combining the reaction product of a mercaptan or mercapto compd. and an org. base with an aldehyde, *e. g.*, mercaptobenzothiazole is heated with di-*o*-tolylguanidine and the product cooled and ground and treated in a closed vessel or under reflux with crotonaldehyde, aldol, acetaldehyde, propionaldehyde or heptaldehyde. Other examples of the manuf. and use of the accelerators also are given. Cf. C. A. 23, 310.

Apparatus for vulcanizing rubber articles. R. W. SNYDER (to Goodyear Tire & Rubber Co.). Brit. 288,248, April 7, 1927. The articles are carried by a conveyer through an approx. U-shaped chamber holding liquid heated by a steam-jacket. Various structural details are described.

Apparatus for vulcanizing rubber articles in successive procession. HARRY E. WANER (to B. F. Goodrich Co.). U. S. 1,693,264, Nov. 27.

Rubber. WILHELM L. UTERMARCK. Fr. 639,961, Aug. 24, 1927. A very durable rubber is obtained by centrifuging latex, treated or not with a small quantity of a non-coagulant such as NH_3 , to obtain a stable latex contg. the rubber, a latex contg. very little rubber which may be used for other purposes and a mud contg. the solid parts of the original latex.

Rubber from plant materials. WILLIAM H. YEANDLE (to Intercontinental Rubber Co.). U. S. 1,695,676, Dec. 18. Rubber-bearing plant material such as guayule shrub is permeated with steam and subjected to increased gaseous pressure and the pressure is then suddenly released to disrupt the plant cells and liberate their contents and facilitate the sepn. of the rubber. An app. is described. Cf. C. A. 22, 2685.

Treating latex. DUNLOP RUBBER CO., LTD., D. F. TWISS and E. A. MURPHY. Brit. 290,313, Nov. 13, 1926. A gentle continuous mixing action is maintained during the concn. by evapn. of latex to which compounding ingredients and stabilizing agents have previously been added. Several examples and formulas are given.

Treating latex. W. A. WILLIAMS. Brit. 289,965, Feb. 7, 1927. In electrodeposition of rubber from latex or the like, an electrolyte which will not readily cause coagulation but will act as a self-excitant between electrodes, is added to the latex, and externally connected electrodes are introduced to effect rubber deposition on the anode, *e. g.*, NH_4Cl in aq. soln. may be added to the latex which may have been preserved with NH_3 and may also be admixed with ZnO and S, etc. The anode may be of Zn and the cathode may comprise a porous pot contg. C and MnO_2 .

Treating latex. W. A. GIBBONS and J. MCGAVACK (to United States Rubber Plantations, Inc.). Brit. 290,242, May 11, 1927. See U. S. 1,673,672 (C. A. 22, 2855).

Rubber compositions. B. W. NORDLANDER (to British Thomson-Houston Co., Ltd.). Brit. 290,602, May 16, 1927. An amorphous compd. of mixt. of S and a stabilizer such as Se or Te is used for vulcanizing rubber. Details are given of prepn. and use of the compn.

Stabilized chlorinated rubber composition. CARLETON ELLIS (to Chadeloid Chemical Co.). U. S. 1,695,641, Dec. 18. Chlorinated rubber contg. not less than about 67% Cl is admixed with $PhNH_2$, toluidine, xylidine, urea or other suitable org. amino antacid.

Apparatus for melting paraffin and mixing it with rubber compositions. ELMER S. WHITTIER (to Fisk Rubber Co.). U. S. 1,696,826, Dec. 25. Structural features.

Porous or spongy rubber. F. RINGER. Brit. 290,447, May 26, 1927. See Fr. 634,694 (C. A. 22, 4007).

Coloring rubber. I. G. FARBERIND. A.-G. Fr. 640,036, Aug. 26, 1927. See Brit. 277,034 (C. A. 22, 2493).

Deodorizing rubber. JEAN L. H. DE G. DE BÉARN. Fr. 640,145, Feb. 7, 1927. Rubber is deodorized by allowing it to remain for several days between 2 layers of finely ground dry charcoal, particularly oak charcoal.

Preserving rubber. ALBERT M. CLIFFORD (to the Goodyear Tire and Rubber Co.). Can. 285,541, Dec. 11, 1928. Naphthalene substituted diamines are used as antioxidants in rubber compds. These materials are prep'd. by the reaction of the naphthols with an alkylene- or an arylenediamine. The reaction products of β -naphthol with ethylene-diamine and with *m*-phenylenediamine are specific examples of the materials which may be used. Cf. C. A. 23, 309.

Rubber articles. EARDLEY HAZELL (to the Dominion Rubber Co., Ltd.). Can. 284,564, Nov. 6, 1928. Rubber articles are manuf'd. directly from latex to which has been added a Zn comp'd. (oxide, hydroxide or any sol. Zn salt dissolved in water or in a soln. contg. NH_4OH in excess) and a soln. of sulfides or polysulfides of Na, K, Li or NH_4 , and depositing rubber from the thus treated latex on a porous form in the shape desired.

Rubber articles. GEORGE G. THORNTON (to the Dunlop Rubber Co., Ltd.). Can. 284,962, Nov. 20, 1928. Rubber articles are formed by depositing the material by electrophoresis on an anodic mold, stripping the deposited material from the mold, placing the material between two surfaces, and vulcanizing by immersing the article in a boiling aq. soln. while permitting the surfaces to move relatively to one another.

Rubber articles manufactured by dipping. GEOFFREY W. TROBRIDGE and EDWARD A. MURPHY (to Dunlop Rubber Co., Ltd.). Can. 284,565, Nov. 6, 1928. A porous mold is dipped into a coagulant (CaCl_2 , AcOH or alum), and afterward dipped into a compounded latex including such materials as ZnO , carbon black and other materials commonly employed in the compounding of rubber. Vulcanizing agents such as S and if desired accelerators of vulcanization may be added to the latex. A suction may be applied to the interior of the porous mold or pressure may be applied to the exterior of the mold. After the dipping process there is removed from that part of the mold farthest from the deposited latex, the coagulant and a part of the water and serum by suction on the interior of the mold. Drying and vulcanization may then be effected, and the article removed. Cf. C. A. 22, 4274.

Rubber conversion products. HARRY L. FISCHER (to the B. F. Goodrich Co.). Can. 284,980, Nov. 20, 1928. Rubber (100 parts) is admixed with 10 parts of catechol and 20 parts of $\text{Ph}_2\text{NH}\cdot\text{HCl}$ and after being thoroughly admixed is placed in a suitable heater maintained at 320° for about 20 hrs. or until conversion is complete. A hard tough material is thereby produced. In general a bath consisting of rubber 100 parts by wt., a phenol 10 to 20 parts and one of the compounds selected from the following empirical class, 20 to 30 parts when treated as above described will yield conversion products. The empirical class includes chlorinated rubber, rubber hydrochloride, rubber sulfur chloride, chlorinated rubber hydrochloride, pinene hydrochloride, $\text{Ph}_2\text{NH}\cdot\text{HCl}$, $\text{Cl}_3\text{C}_6\text{H}_2\text{NH}_2\cdot\text{HCl}$, *m*- $\text{O}_2\text{NC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$, HgCl_2 , SnCl_4 , naphthalene tetrachloride, Ph_3CCl , ZnBr_2 , HgBr_2 , rubber dibromide, $\text{Ph}_2\text{NH}\cdot\text{HBr}$, CdSO_4 , $\text{Al}_2(\text{SO}_4)_3$, HgSO_4 , $\text{Ph}_2\text{NH}\cdot\text{H}_2\text{SO}_4$ and $\text{PhNH}_2\cdot\text{Cl}_3\text{CCO}_2\text{H}$.

Rubber conversion products. HARRY L. FISHER (to the B. F. Goodrich Co.). Can. 284,981, Nov. 20, 1928. Conversion products of rubber are produced by forming a liquid admixt. of rubber, a rubber solvent, a phenol and a substance selected from a class comprising HCl , HBr , $\text{CCl}_3\text{CO}_2\text{H}$, dil. H_2SO_4 , org. sulfonic acids, and org. sulfonyl chlorides, and heating the admixt. at approx. the boiling temp. for an extended period, preferably under reflux to prevent loss of solvent in the admixt.

Rubber threads. MAX DRAEMANN and MAX BÜHLING. Fr. 640,179, Aug. 9, 1927. An app. is described for making threads of rubber by pressure of the rubber through perforated plates.

Artificial threads from chlorinated rubber. CARLETON ELLIS (to Chadeloid Chemical Co.). U. S. 1,695,643, Dec. 18. A concd. soln. of chlorinated rubber is formed into filaments (suitable by extrusion through as fine orifice) and the solvent is removed. The product may be used for making fabrics.

Increasing the plasticity of rubber. CARLETON ELLIS (to Chadeloid Chemical Co.). U. S. 1,695,636, Dec. 18. Rubber is given an increased plasticity without dissolving it, by incorporating with the unvulcanized rubber a quantity of an aromatic solvent such as C_6H_6 , which is not greater than the quantity of the rubber and then treating the

material with Cl under pressure to effect chlorination to a stage above heptachloro-rubber.

Adhesive comprising chlorinated rubber. CARLETON ELLIS (to Chadeloid Chemical Co.). U. S. 1,695,637, Dec. 18. Chlorinated rubber is used with a solvent such as CS_2 or C_6H_6 to form an adhesive which is suitable for various purposes.

Splicing ends of rubber tubes to form tire tubes, etc. JOHN P. COE (to G. & J. Tire Co.). U. S. 1,693,636-7, Dec. 4.

Manufacture of rubber tires for vehicles. ERNEST HIBBERT (to Hibbert Pneumatic Cell Tyre Co., Ltd.). U. S. 1,694,260, Dec. 4. Mech. features.

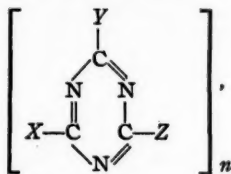
Waste rubber. COGEDEX (COMPAGNIE GÉNÉRALE D'EXPLOITATION) SOCIÉTÉ ANON. Fr. 640,332, Aug. 31, 1927. Waste rubber is powdered and mixed with latex, which acts as a solvent and plastifying agent. S is added and the mass vulcanized.

Rubber substitute. ROGER A. L. SELIGMAN. Fr. 640,147, Feb. 7, 1927. Asbestos is intimately mixed into a soln. of rubber and the solvent evapd. The asbestos is preferably treated with S and heated to about 150° in the absence of O before mixing.

Apparatus for vulcanizing tire casings or similar articles. HENRY WILLSHAW (to Dunlop Tire and Rubber Corp. of America). U. S. 1,695,835, Dec. 18.

Vulcanizing rubber. IWAN OSTROMUISLENSKII (to Revere Rubber Co.). U. S. 1,696,409, Dec. 25. Vulcanization without S is effected in the presence of org. nitro compds. such as 1,3,5-trinitrobenzene by combining the rubber with a nitrobenzene and with C black or other element of the C group and then effecting the vulcanization.

Vulcanizing rubber. SOC. ANON POUR L'IND. CHIM. A BALE. Brit. 290,178, May 7, 1927. Vulcanization is effected in the presence of various compds. of the general formula,



in which X and Y are any residues, and Z is a H atom or a radical connected with the C atom by N, O or S.

Vulcanization of rubber. THE INDIA RUBBER, GUTTA PERCHA & TELEGRAPH WORKS CO., LTD. Fr. 640,615, Aug. 1, 1927. In the vulcanization of rubber coverings for rollers, etc., the roller is surrounded with a heating fluid and the interior is independently supplied with a heating fluid. The exterior is treated with hot water under pressure, while steam at a higher temp. is circulated through the interior.

Imitation patent leather. ROBERT C. HARTONG (to Seiberling Rubber Co.). U. S. 1,694,258, Dec. 4. A rubber compn. is calendered upon a smooth surface such as a metal sheet capable of transferring its surface effects to the compn., a textile material frictioned with a rubber compn. is doubled upon the first-mentioned compn., and the product is vulcanized.

Catgut substitutes. DUNLOP RUBBER CO. Swiss 126,171, Nov. 24, 1926. See Brit. 264,640 (C. A. 22, 165).

Rubber. THE ANODE RUBBER CO., LTD. Swiss 127,539, May 17, 1926. Rubber objects are prepd. from an aq. rubber dispersion by means of a water-permeable mold in which the rubber is deposited, a conglomerating agent being employed.

Forming deposits of latex, etc. COMPAGNIE GÉNÉRALE D'ÉLECTRICITÉ (to Anode Rubber Co. (England), Ltd.). Brit. 291,339, May 27, 1927. Gel-forming substances are added to latex or like suspensions or solns. and the mixt. is subjected to conditions which will form a gel. Gelatin, agar-agar, carrageen moss or albumin and $ZnCl_2$ are among the substances which may be used. Heating or cooling may also be used for effecting gelling, and the process may be applied to the formation of shaped articles of ceramic material, hard rubber and papier mache. Porous molds may be used and various details and modifications are described.

Treating latex. COMPAGNIE GÉNÉRALE D'ÉLECTRICITÉ (to Anode Rubber Co. (England), Ltd.). Brit. 291,805, June 9, 1927. Aq. rubber dispersions are made viscous (to facilitate dipping, spreading or spraying) by adding polysaccharides, albuminoids or plant exts., such as gum arabic, which form viscous solns. but not jellies, or such as starch, gelatin or agar-agar which normally form jellies but are partially hydrolyzed to destroy this property. NH_3 or amines present in the latex treated may serve as hydrolyzing agents.

Preserving rubber latex. JOHN MCGAVACK and ROY A. SHIVE (to Naugatuck Chemical Co.). U. S. 1,699,368, Jan. 15. A stable uncoagulated rubber latex having a p_H of between 7 and 4.5 contains an org. preservative such as a sulfonic reaction product of cinnamic acid and BuOH capable of exerting its effect on both sides of neutrality. U. S. 1,699,369 specifies treating latex with a sulfonic alkyl aryl reaction product such as a sulfonic reaction product of BuOH and cinnamic acid together with CH_3O to prepare a stable product having a p_H less than 7. Cf. C. A. 23, 731.

Preserving rubber. SILESIA VEREIN CHEMISCHER FABRIKEN. Brit. 291,431, June 2, 1927. Aging is retarded by adding to rubber reaction products formed by reaction between polyhydroxyaldehydes such as aldoses, polysaccharides as milk sugar or hydrolyzed products such as glucose or invert sugar, and amines such as aniline, α - and β -naphthylamine, *m*-toluylenediamine, urea or *p*-aminophenol.

Treating rubber films. CARL PLAAT. U. S. 1,698,275, Jan. 8. Rubber films are subjected to the frictional action of a narrow rotary surface such as two rolls of different speeds in order to produce ornamental effects.

Forming hollow rubber articles. DUNLOP RUBBER CO., D. F. TWISS AND E. A. MURPHY. Brit. 291,479, Dec. 4, 1926. A fusible or sol. former is dipped in natural or artificial rubber dispersion, drying and vulcanization are effected, and the former (which may be made of fusible metal, wax or mixts. of S and other suitable materials) is removed at any time after drying has been at least partially effected.

Rubber articles. THE ANODE RUBBER CO., LTD. Fr. 642,183, Oct. 11, 1927. The molds for molding latex mixed with fillers, etc., are coated with gelatin, etc., contg. a coagulant such as Na_2SiF_6 , AcOH or a salt of Ca, Mg, Zn or Al. The mold is agitated to make the coating more uniform.

Baseball centers. MILTON B. REACH (to A. J. Reach Co.). U. S. reissue 17,200, Jan. 22. Two hollow hemispheres of rubber compn. are vulcanized, a cork sphere is enclosed between them and the materials are vulcanized together with an interposed layer of quick-curing rubber compn. (The original pat. No. 1,530,410 was issued March 17, 1925.)

Electrodeposition of rubber. S. O. COWPER-COLES. Brit. 291,471, Nov. 20, 1926. Electrophoretic deposition of rubber from aq. dispersions is effected intermittently, to permit of disposal of any gas bubbles which have formed. The anode may be caused to rotate or to vibrate during the deposition. Metal molds may be used such as Cd or Zn or Zn-coated Fe or Al which may be dipped in adhesive such as gum arabic or gum tragacanth or coated with plumbago, French chalk, etc. Coloring, "compounding" or vulcanizing substances may be added, and various details of operation are given.

Coating wires, threads or filaments with rubber, etc. DUNLOP RUBBER CO., LTD., D. F. TWISS AND E. A. MURPHY. Brit. 291,485, Jan. 28, 1927. The material is passed through a bath contg. a concd. and compounded aq. dispersion, in the form of a cream or viscid fluid contg. rubber, gutta percha, balata or the like, and the uniform coating thus applied is dried without allowing it to contact with any foreign body. The coating may be vulcanized. An app. is described and numerous formulas and details for prepg. compns. are given.

Uniting metals in layers with rubberized fabrics. HAROLD GRAY (to B. F. Goodrich Co.). U. S. 1,697,275, Jan. 1. The surface of material such as steel or other metals to be united with rubberized fabric is coated with a film of a reaction product of turpentine with a substance such as trichloroacetic acid, S chloride or $SnSO_4$, comprising either a strong inorg. non-oxidizing acid or a compd. which by thermal or hydrolytic dissocn. will give such an acid and the materials are assembled under pressure with the coated surfaces in contact.

Rubber substitute. JEAN BAER. Fr. 640,967, Sept. 14, 1927. An elastic material resembling rubber is obtained by the action of S or S yielding substances on saturated halogenated hydrocarbons of the group C_nH_{2n+2} such as CH_3Cl , CH_3Br , CH_3I , C_2H_5Cl , C_2H_5Br , etc., or mixts. thereof in the presence of an aq. alk. or alc. solvent.

Apparatus for vulcanizing tires. DUNLOP RUBBER CO., LTD., H. WILLSHAW, T. NORCROSS AND F. G. BROADBENT. Brit. 291,905, March 19, 1927. Structural features.

Mold for vulcanizing tires. CLAUDE A. WITTER. U. S. 1,697,703, Jan. 1. Structural features.

Rubber vulcanization. METALLBANK UND METALLURGISCHE GES. A.-G. Brit. 291,438, June 2, 1927. Org. Se compds. (such as those which may be obtained by reaction between H_2Se , NH_3 and benzaldehyde or other suitable aldehyde) are used as accelerators.

Vulcanizing rubber. WILLIAM P. TER HORST (to Rubber Service Laboratories

Co.). U. S. 1,698,569, Jan. 8. Phenylpiperidylguanidine is used as an accelerator and other similar compds. also may be used. Cf. C. A. 22, 2685-6.

Vulcanization of rubber. THE NAUGATUCK CHEMICAL COMPANY. Fr. 642,264, Oct. 14, 1927. Vulcanization is accelerated by means of a halogen-contg. or other deriv. of the condensation product of an aliphatic aldehyde having 2-7 C atoms in the mol. with a primary amine. In an example a soln. of the condensation product of hept-aldehyde and PhNH_2 in C_6H_6 or CCl_4 is treated with Cl until HCl begins to be evolved; the product contains 26.4% of Cl. Other examples of the prepn. of suitable derivs. of the same condensation product are given.

Rubber vulcanization. SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,698,712, Jan. 15. A rubber compn. is prepd. contg. a metal compd. such as ZnO together with S and a CS_2 -contg. material or deriv. such as hydroxybutyl thiocarbonic acid disulfide and a second compn. is also prepd. contg. rubber, a metal compd. such as ZnO together with S and dibenzylamine or other suitable amine. One of these compns. also contains a material such as phthalic anhydride which will check the vulcanizing action of ingredients associated with the rubber. The compns. are brought together in the form of plies and the amine and CS_2 -contg. material are permitted to diffuse throughout the compns. and vulcanization is effected. U. S. 1,698,713, specifies control of vulcanization by prepg. a cement comprising rubber, a Zn compd. such as ZnO, a S-contg. material such as S itself, a CS_2 -contg. material or deriv. such as normal butylthiocarbonic acid disulfide, together with phthalic anhydride and C_6H_6 . When it is desired to effect vulcanization, aniline is added in excess of that required to counteract the checking effect of the phthalic anhydride. U. S. 1,698,714 specifies controlling vulcanization by treating vulcanized rubber contg. hydroxybutylthiocarbonic acid disulfide or other accelerating ingredient with a material such as NH_3 which will check the functioning of the accelerating ingredient. U. S. 1,698,715 specifies causing a vulcanizing ingredient contained in rubber to react with a substance such as phthalic anhydride for checking the vulcanizing function of the ingredient and then, when desired, adding an agent such as PhNH_2 which will cause vulcanization. Numerous examples and details are given. Cf. C. A. 22, 2856.

Rubber latex. THE NAUGATUCK CHEMICAL Co. Fr. 643,122, Oct. 18, 1927. See Brit. 282,011 (C. A. 22, 3805).

Treating rubber latex. SOCIETÀ ITALIANA PIRELLI. Brit. 292,964, June 27, 1927. Latex is rendered coagulable by heat by addn. of oxides or hydrates of bi- and trivalent metals such as Zn, Mg, Al or Ca and a salt of NH_4 such as the sulfate. Salts of the same metals also may be added, and the treated latex may be used for the direct production of rubber articles. Cf. C. A. 22, 4877.

Deposition of rubber from latex. W. A. WILLIAMS. Brit. 293,095, March 28, 1927. In effecting deposition from material such as ammoniacal latex, there is added a salt of the metal employed as anode, e. g., ZnSO_4 when Zn electrodes are used. Various other details are described. Cf. C. A. 23, 547.

Rubber compositions. SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,701,946, Feb. 12. Rubber is admixed with 2 or more of the ingredients: dibenzylamine, CS_2 or a material contg. CS_2 such as "oxy-*n*-butylthiocarbonic acid disulfide," (di-Bu ester of dithiobis [thionoformic acid]) Zn in combination such as ZnO and S, and then, substantially without change of form, the remainder of the vulcanizing ingredients are introduced from soln. The dibenzylamine and CS_2 are always separately introduced.

Coating composition containing rubber. CHARLES M. A. STINE and JAMES E. BOOGE (to E. I. du Pont de Nemours & Co.). U. S. 1,700,779, Feb. 5. In order to form a rubber-contg. coating on metals or other materials, a mixt. comprising rubber, a volatile thinner such as benzine and a Co, Mn, Pb, Zn or other suitable metal drier is applied to the surface and is exposed to the air and heated to cure the rubber by the action of the drier and evapn. of the thinner. Cf. C. A. 22, 1705.

Hard rubber coating composition. SAMUEL E. SHEPPARD and JOHN J. SCHMITT (to Eastman Kodak Co.). U. S. 1,701,129, Feb. 5. Commminuted hard rubber is digested in an aq. NaOH soln. for 2-5 hrs., the alkali is washed out and the treated material is dried and is incorporated with a molten flux comprising rosin and China wood oil and heated at 200-250° to produce a homogeneous fusion product; the latter is then dissolved in three times its quantity of a solvent such as benzene and coal tar naphtha to form a compn. suitable for spray-coating of metal.

Rubber articles reinforced with long fibrous material. WILLIAM B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,702,225, Feb. 12. In forming material for shoe soles or other articles, relatively long fibers such as cotton or ramie impregnated with latex rubber are distributed through a rubber compn. by milling.

Drying rubber articles. P. KLEIN (to Anode Rubber Co., Ltd.). Brit. 293,061, Jan. 25, 1927. Shaped articles of substantial thickness produced by immersing a former in an aq. dispersion of rubber or the like are dried by maintaining one side at a higher temp. and permitting escape of water from the other side on which an impervious skin is prevented from forming until the drying is completed. The articles may be dried on metal molds heated by elec. resistances or by induction. Various details and modifications of procedure are given and the process is applicable to *cellulose esters, natural or synthetic resins, casein or albumin compns.*, etc.

Roughened or ornamental surface on rubber articles. S. D. SUTTON and VEEDIP, LTD. Brit. 293,111, March 30, 1927. A final coating of concd. latex is partially dried, treated with a solvent, and then further dried. Various details and modifications are given.

Variiegated markings on rubber surfaces. DUNLOP RUBBER Co., LTD. and G. G. THORNTON. Brit. 292,704, March 29, 1927. Irregular embossed markings are produced on surfaces such as rubber by deposition from aq. dispersions, by placing the articles between 2 surfaces such as metal and vulcanizing in boiling water or an aq. soln.

Rubber sheets with grain-like markings. C. MACINTOSH & Co., LTD., S. A. BRAZIER and G. F. THOMPSON. Brit. 292,754, May 26, 1927. Sheets of rubber are coated with a rubber soln. of different color, assembled into blocks (which may be deformed under pressure) and the blocks are sliced.

Artificial rubber. I. G. FARBENIND. A.-G. Brit. 292,103, June 13, 1927. Polymerization of di-olefins emulsified in suitable liquids (such as aq. emulsions which may contain proteids, milk, dextrin, soaps or sulfonates) is effected by the use of H_2O_2 with or without other polymerizing agents, buffer mixts., etc.

Molds (of aluminum or aluminum alloy) for molding rubber tires. H. A. BRIT-TAIN (to Goodyear Tire & Rubber Co.). Brit. 292,905, June 25, 1927. Mech. features. **Rubber-masticating apparatus.** PARK E. WELTON. U. S. 1,701,832, Feb. 12.

Waste rubber. THE DUNLOP RUBBER Co., LTD. Fr. 643,357, Nov. 4, 1927. Waste rubber is reduced to small pieces mixed with 1-3% of pure S and $\frac{1}{2}$ to 3% of an antioxidant, the whole being vulcanized under pressure. As antioxidant, quinol, aminophenol, diaminophenol, aldol, naphthylamine or condensation products of aldehydes and aromatic amines may be used.

Refining reclaimed rubber. JOHN F. FISHER and WALLACE R. GILLAM (to Philadelphia Rubber Works Co.). U. S. 1,700,287, Jan. 29. The rubber is passed through a mill to form it into a continuous sheet, divided lengthwise into strips to sep. stocks of different grades contained in the sheet, and the stock of one grade is fed back into the mill substantially in constant ratio to the feeding of new stock into the mill. An app. is described.

Tennis balls. C. MACINTOSH & Co., LTD., S. A. BRAZIER and L. R. RIDGWAY. Brit. 293,124, April 1, 1927. A cloth-covered tennis ball is treated by immersion or otherwise with a rubber or gutta percha soln. and is afterwards vulcanized, preferably with use of an accelerator of the dithiocarbamate or xanthate class.

Accelerator for vulcanization. JAN TEPPERMA (to The Goodyear Tire and Rubber Co.). Can. 286,105, Jan. 1, 1929. Rubber is vulcanized by heating a mixt. contg. rubber, S and a reaction product of mercaptobenzoxazole and a basic N compd. contg. at least two hydrocarbon groups. Cf. C. A. 22, 2494.

Color Reactions of Rubber and Gutta-Percha*

F. Kirchhof

THE present paper was suggested by a recent publication of Pauly¹ on the same subject, who applied the well known sterol reactions of Hesse, Liebermann, Tschugajeff, etc., to the hydrocarbons of rubber and gutta-percha. These reactions depend either upon the action of concentrated H_2SO_4 on chloroform solutions of the substances in the presence or absence of acetic anhydride (Liebermann, Burchard and Hesse reactions) or other solvents, or condensation reagents are used, such as acetyl chloride and zinc chloride by Tschugajeff, and acetic acid with arsenic trichloride by Kahlenberg, and trichloroacetic acid with a trace of formaldehyde by Godoletz.

All the known sterol reactions take place also with rubber or gutta-percha, with the appearance of intense red or violet colorations of varying stability, the color depending in part upon the quality and in part upon the purity of the samples.

The Burchard reaction in particular is very sensitive in these respects. Thus with rubber purified with alkali by the Pummerer method, the color is a Bordeaux red which does not change for a long time, whereas solutions of unpurified rubber change rapidly, a change which is rightly ascribed by Pauly to relatively rapid oxidation in the presence of oxidation products in the case of the unpurified rubber.

All changes in rubber brought about by concentrated sulfuric acid depend upon the formation of sulfo-acid cyclorubbers, as numerous earlier researches of Kirchhof² and others have shown, a fact which is apparently not known by Pauly.

This applies also to the reactions with hot trichloroacetic acid, as shown by patents of the Goodrich company, data which I was able to confirm. With rubber or gutta-percha and trichloroacetic

*Reprinted after translation from *Kautschuk*, Vol. 4, No. 9, pp. 190-192 (1928).

Weber Color Reactions of Various Rubber Hydrocarbons and Some Other Substances

SUBSTANCE	COLOR OF BROMIDE	COLOR OF PHENOL FUSION MIXTURE	COLOR OF FRESH SOLUTION OF FUSION MIXTURE IN		
			CHLOROFORM	CARBON TETRACHLORIDE	ETHER
Pure rubber (Ceylon crepe)	yellowish-white	blue-violet	blue-violet	blue-violet	yellow
Pure gutta-percha (Tjipetr)	white	blue	blue	blue-violet	yellow
Oxidized gutta-percha	yellowish-white	carmine-red	carmine-red	carmine-red	yellow
Synthetic rubber II	yellowish-white	cherry-red	cherry-red	cherry-red	yellow
Sulfocyclorubber	yellowish-brown	carmine-red	cherry-red	cherry-red	yellow
Trichloroacetic acid-rubber	light yellow	reddish-brown	reddish-brown	reddish-brown	yellow
Rosin oil	light brown	reddish-brown	reddish-yellow	reddish-yellow	brown
Rosin	light brown	reddish-yellow	reddish-yellow	reddish-yellow	brown

acid, the fused mixture becomes yellowish-red, and on raising the temperature to the boiling point (195-196° C.) the color becomes an intense dark orange-red. On solution of this fusion mixture in water a gray-violet precipitate settles out, which on exposure to air acquires a yellow-ochre color. When the precipitate is dried out of contact of the air, a yellowish-white powder is obtained, which added to fused trichloroacetic acid forms again a reddish-yellow solution.

This fusion mixture has then all the aspects of a colloidal solution of isomeric rubber hydrocarbon, which has been termed trichloroacetic acid-rubber, and the behavior of which indicates that it is related to the metal halide rubbers of Bruson.

The bromide of this isomeric rubber was a light yellow powder partially soluble in alcohol. In order to avoid oxidation of the readily oxidized isorubber, it was prepared by direct bromination in trichloroacetic acid.

Trichloroacetic acid has then an isomerizing action on rubber similar to that of concentrated sulfuric acid. Since trichloroacetic acid also gives characteristic color reactions with a series of other unsaturated cyclic hydrocarbons, the Tschugajeff-Godoletz reaction and similar reactions probably involve transitory addition of the trichloroacetic acid (or sulfuric acid) onto the free bonds, with formation of cyclorubbers, which, because of their colloidal state at the moment of formation, show an intense coloration. By solution of the trichloroacetic acid fusion mixture in water, there appears a turbidity and then a separation of the isomeric rubber in flocculent form.

The appearance of these colors cannot therefore be considered to be a proof of the original existence of a ring structure in the rubber hydrocarbon, as assumed by Pauly, but as a result of cyclization or

a rearrangement in the rubber molecule during the reaction.

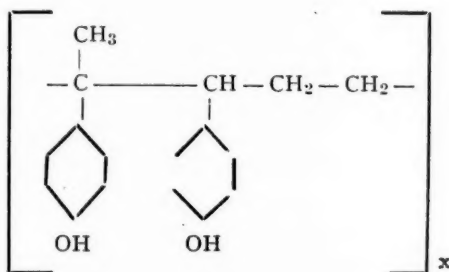
The relatively great tendency of rubber hydrocarbons toward cyclization is accordingly the cause of the colorations in these reactions.

Much more characteristic and older, though unfortunately little known, is another color reaction of rubber hydrocarbons. It was first observed by Weber³ in 1900 when he applied the Friedel-Crafts reaction to rubber dibromide $(C_5H_8Br_2)_x$. This reaction depends upon a conversion of halogen-hydrocarbons with phenols in the presence of catalysts, *e. g.*, $AlCl_3$.

The characteristic color reaction of rubber dibromide, *i. e.*, an intense blue to red-violet, does not appear in the presence of catalysts such as $AlCl_3$, $FeCl_3$ or $ZnCl_2$, for in this case the fusion mixture is yellowish brown. This may account for the fact that this color reaction has often been overlooked.

Weber succeeded in isolating from the yellow-brown fusion mixture a substance of the composition $[C_5H_8(OC_6H_5)_2]_x$, which was soluble in alkalis. Since, according to Weber, phenolic ethers do not under the same conditions react with rubber bromide, he concluded that it was not the *p*-hydrogen atom of the phenyl group but that of the hydroxyl group which reacts with the bromine atom of the dibromide, with formation of ether-like phenol compounds of rubbers. Only recently did Fisher, Gray and McCollm⁴ repeat the experiments and show that the hydrogen atoms of the hydroxyl group are replaceable by methyl groups, and therefore that the reaction takes place between bromine and the *p*-hydrogen of the phenols.

In this transformation, accordingly, no phenyl ether of the rubber hydrocarbon is obtained, but hydroxyphenyl derivatives of hydro-rubber of the following constitution:



This constitution explains, among other things, their solubility in alkalis.⁵ These hydroxyphenyl derivatives have, as already mentioned, a brown color. In the absence of catalysts and with relatively pure reagents, splendid blue to red-violet colored fusion mixtures are obtained, the color being stable for several days. The fusion mixtures change color when poured into organic solvents. Thus in ether the violet color changes to yellow-brown, in acetic anhydride to reddish-brown, while in chloroform and in carbon tetrachloride the original color remains unchanged for a long time, but ultimately changes to green, to greenish-brown, and finally to brown, with separation of a brown flocculent precipitate.

The characteristic violet color of the phenol fusion mixtures of the bromides of rubber and gutta-percha in the absence of catalysts, which may appropriately be called the *Weber color reaction*, is to all appearances a typical dispersion color reaction depending primarily upon the size of the dispersed particles. This size depends in turn upon the concentration, temperature and occurrences of secondary chemical reactions. On this basis the natural impurities in rubber (oxidation products) also play a part, under which conditions the blue-violet color of the fusion mixture of the pure bromide becomes red-violet or cherry-red. The latter color is also observed with the bromide of sulfocyclorubber, as shown in the table.

To what extent these various color reactions allow conclusions on the constitution of rubbers is left in doubt, but they do permit an estimate of the purity of a sample.

Technique and Sensitivity of the Weber Reaction

After preliminary extraction with acetone, swell or dissolve a few cubic centimeters of finely divided sample (in which rubber or gutta-percha is to be identified) in carbon tetrachloride and brominate in this liquid. To this end suspend a few milligrams of the bromide in 2-3 cc. of carbon tetrachloride, add 1-2 cc. of highly concentrated phenol solution (or the corresponding quantity of crystallized phenol), warm gently, to distil off the CCl_4 and then heat gradually to the boiling point. If rubber or gutta-percha is present, the fusion mixture acquires a characteristic blue to red-violet color.

A few drops of the mixture may be poured into various organic solvents, *e. g.*, chloroform, ether or acetic anhydride, and the new color observed (see Table).

It is interesting to note that hexahydrophenol (cyclohexanol) and phenetole do not give the characteristic violet color, but only a yellow-brown color, which with phenetole appears only slowly.

On the other hand, when heated with pyrogallol, rubber dibromide gives a cherry red color and with resorcinol a dark orange-red or shellac color. Like the violet phenol fusion mixtures, these fusion mixtures are soluble in alcoholic potassium hydroxide, giving intense yellow-brown solutions (potassium salts of the corresponding hydroxyphenyl hydorrubbers). None of these last named fusion mixtures has so characteristic a color as the phenol fusion mixtures of the dibromides of rubber, gutta-percha and balata.

BIBLIOGRAPHY

- (1) *J. prakt. Chem.* 118, 48 (1928).
The Rubber Age (N. Y.) 23, 259 (1928).
Rubber Chemistry and Technology 1, 361 (1928).
- (2) *Kautschuk* 4, 142 (1928).
- (3) *Berichte* 33, 791 (1900).
- (4) *J. Am. Chem. Soc.* 48, 1309 (1926).
- (5) Geiger, *Helvetica chim. acta* 10, 530 (1927).

Some New Laboratory Work on Rubber

A. A. Somerville and J. M. Ball

CRUDE rubber is not of much use commercially or industrially until after it has been put through a chemical process discovered by Charles Goodyear: that of adding sulphur and heating. But sulphur is not the only material that can be used to change and improve the natural physical properties of raw rubber. There are other things than sulphur that are beneficial, one of which is Selenium.

It is a pleasure to be permitted to talk here in Boston before a meeting of the North-eastern Section of the American Chemical Society and the Boston Rubber Group, devoted at this time particularly to the subject of rubber. It is a privilege to be permitted to talk on the subject of Selenium at this meeting because it is coming back very close to the home of Selenium so far as it is associated with the rubber industry.

The question I want to discuss is this: Did C. R. Boggs of the Simplex Wire & Cable Company discover anything

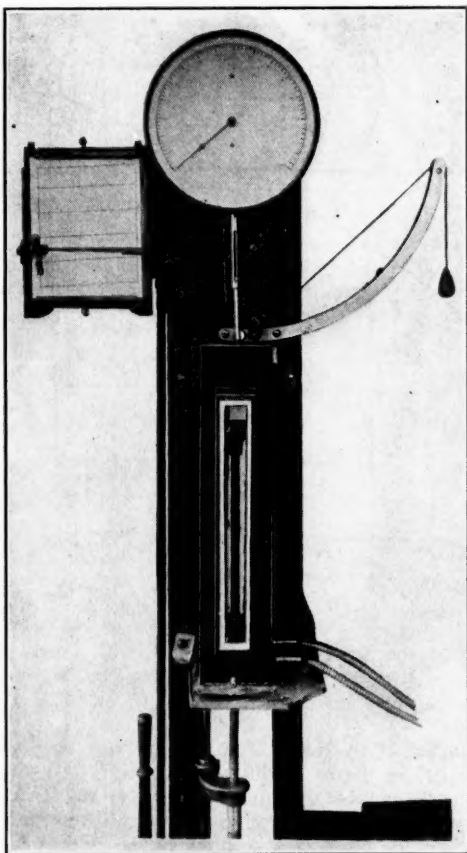


Fig. 1

NOTE.—Paper read before the N. E. Section A. C. S. and the Boston Group, Rubber Division, A. C. S., January 12, 1929, at Boston, Mass.

that is of any real commercial importance or value to the rubber industry when he did his first work on Selenium in connection with rubber? In answer to that question I want to tell you about some of the laboratory work that has been done this past year (1928) on the use of Selenium in rubber.

Last September in talking before the Rubber Division of the A. C. S. at Swampscott, Mass., an attempt was made to show that when tests are made on rubber at both 0° and 100° C. the best results are obtained when about 2 or 3 per cent of sulphur is used on the rubber; also that overcures show up much more prominently when the stock is tested at 100° than when the stock is tested at 0° . Pictures were shown of a testing machine equipped for making stress-strain tests at 0° and 100° , and also pictures showing the spread between the stress-strain curves of ordinary rubber compounds when tested at 0° and 100° .

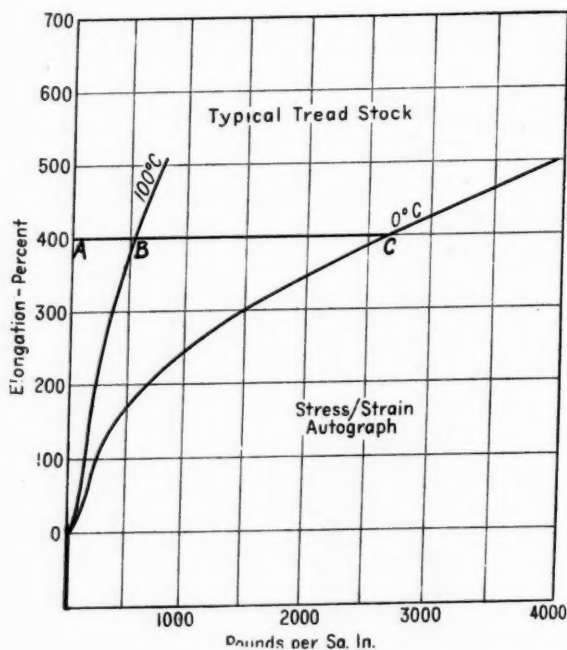


Fig. 2

In Figure 1 is shown the Scott machine equipped with a tank to hold water so arranged that the rubber test piece can be stretched in the water at a temperature approximately either 0° or 100° , that is, freezing or boiling.

If samples of rubber in the form of a circular test ring are stretched at 0° and 100° by means of this machine, what is known as a stress-strain curve can be drawn automatically, and if the curves are drawn at different temperatures on samples cut from the same sheet of stock, the position or location of the stress-strain curves varies according to the temperature. The stress-strain curves drawn for an ordinary tire tread are shown in Figure 2.

It was also shown that if a stock is overcured it may still give

a splendid test at 0° or at room temperature, but when tested at 100° C. it breaks exceedingly short, as is indicated in Figure 3.

Those last two figures show what was merely a diagnosis of an

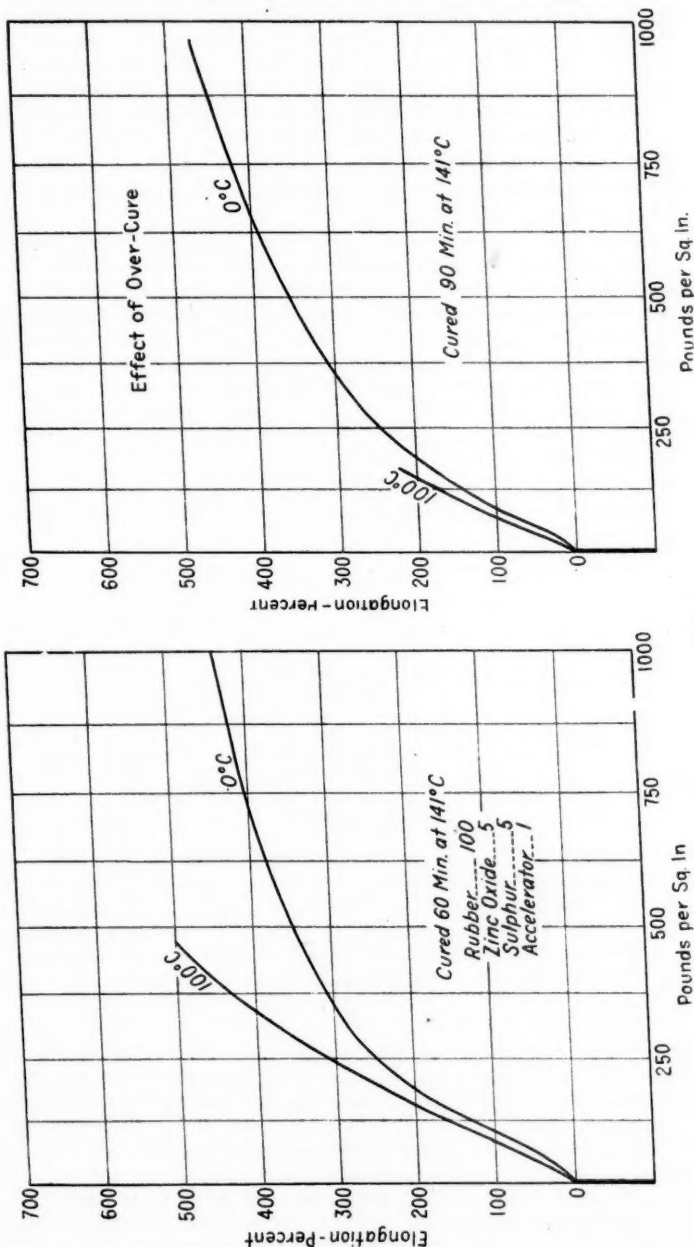


Fig. 3

existing condition which might be termed one of the ills of present rubber goods compounding. There was nothing said at that time

with reference to prescribing a remedy or medicine to overcome the ill.

It would seem that it might be highly desirable to bring those two 0° and 100° stress-strain curves more closely together; in other words, to make a rubber compound that would test nearly the same at either 0° or 100°. It is quite possible to make compounds having such properties that the stress-strain curves drawn at 0° and 100° actually cross—where the stress at 100° is actually higher than at 0° at certain elongations of the rubber test piece.

The compound producing the curves shown in Figure 4 consists of rubber, together with small amounts of zinc oxide, sulphur, stearic acid, accelerator and Selenium.

There are, I believe, three distinct ways of making rubber compounds that will, when tested at 0° and 100°, show a crossing of the stress-strain curves. It can be accomplished in the case of the so-called pure gum stocks by using a very small amount of sulphur, 1 per cent to 1½ per cent on the rubber, and driving that sulphur home by a big amount of accelerator. Such stocks are not claimed to be particularly good for any purpose, though they can be made to show a crossing of the 0° and 100° stress-strain curves. At the same time there is great danger of overcuring, and of either having the stock break extremely short at 100° C. or of suffering reversion and consequent softening of the stock.

A second method of making a stock that will give a crossing of

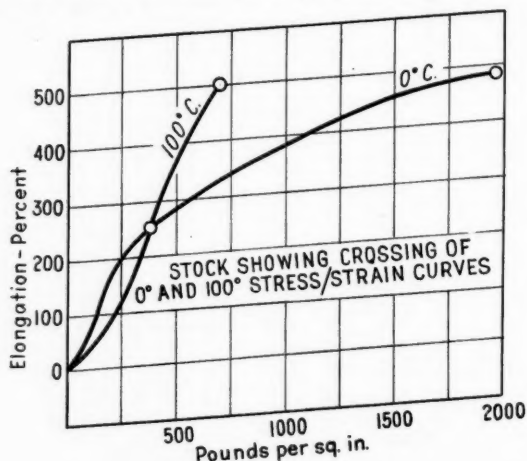


Fig. 4

the 0° and 100° stress-strain curves is to use tetra-methyl-thiuram-disulphide as a vulcanizing agent, using it to replace both the sulphur and accelerator ordinarily used. Such a compound is unusually expensive although it should also be said that it has most unusual heat aging qualities, and will stand an unusually long cure without being overcured or without breaking short when tested hot.

The third method of producing this crossing of the 0° and 100° stress-strain curves, the one which so far has been found to be the surest, most practical, and most effective, is by the use of Selenium used as a secondary vulcanizing agent, in addition to a low amount of sulphur and the ordinary organic accelerator—and it is data on

Selenium compounded samples made in several different rubber laboratories or factories that will be shown to you.

It would be desirable to know the elongation to which a rubber article is ordinarily stretched in service whether that article is a tire, belt or shoe, or any part of the tire, belt, or shoe. That is something that is not known, but we do know that these 0° and 100° stress-strain curves can be regulated to cross each other at any elongation from 100 per cent to 400 per cent, depending upon the compounding and the cure given.

In Figure 5 are shown the stress-strain curves at 0° and 100° on one compound given three different cures, and you will note that the crossing of those two stress-strain curves occurs at different elongations as the cure progresses.

It should be said that we have not been able to make high stress-strain heavily compounded stocks, such as tire treads, that will show a crossing of the 0° and 100° stress-strain curves.

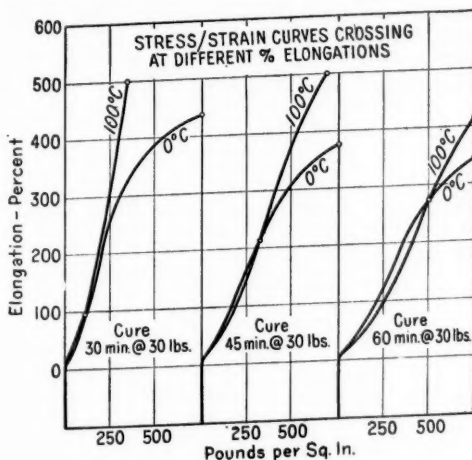


Fig. 5

Last September at Swampscott it was shown that if a strip of belt an inch in width, such as this sample in my hand, is stripped or the adjacent plies of fabric pulled apart by the usual machine method of making what is known as a friction stripping test, the pull in pounds necessary to separate adjacent plies varies according to the temperature. As the temperature increases from 0° to 100° C. the pull in pounds to strip the belt ordinarily decreases, usually as much as 10 per cent to 20 per cent in high grade belts and 25 per cent to 50 per cent in second or third grade belts. In Figure 6 is shown such a test at 0°, 25° and 100° drawn automatically on the testing machine. The same data averaged is shown in another form in Figure 7.

You have previously been told that an overcured stock shows up poorly when tested at high temperatures such as 100° C. That can be shown very readily in the case of stripping a belt sample. In Figure 8 you are shown friction stripping tests at 0°, 25° and 100° on samples of belting given two different cures, one sample having had what we will term a proper cure and the other sample having had a 50 per cent longer cure. The stripping test is the same at 0°

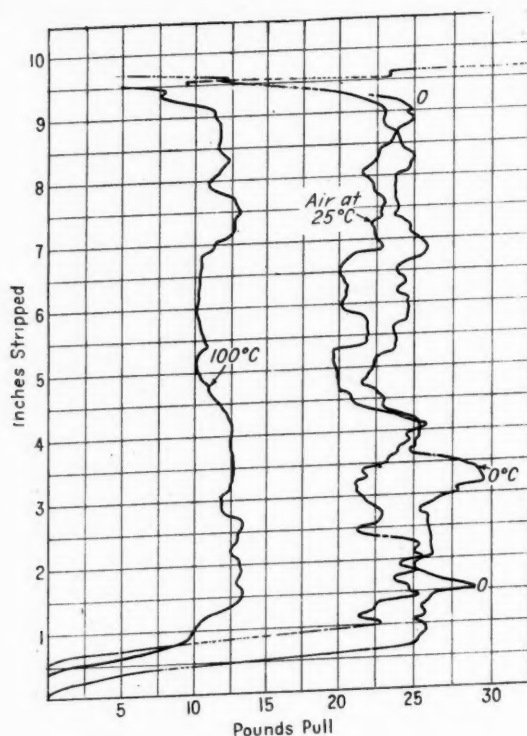


Fig. 6

or 25° on both cures, but in the overcure when tested at 100° the stripping test falls down badly, while in the good cure the stripping test is nearly as high at 100° as at 0°, and it would do well to add here that friction stocks can be made which will show a higher stripping strength at 100° than at 0° C.

Many technically trained rubber men will say today that this old style friction stripping or pulling test is not indicative of the service

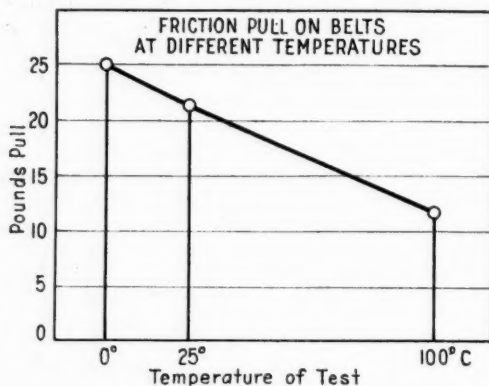


Fig. 7

that a rubberized fabric article such as a belt or tire will give in actual practice, but that a more informative test is that made possible through the use of so-called flexing machines such as that developed by the United States Rubber Company, and now manufactured commercially by Henry L. Scott Company at Providence, R. I. A picture of that machine is shown in Figure 9.

About a year ago three rubber companies very kindly made up belt samples, using two compounds, the same except that one contained an added amount of Selenium, cured those stocks, determined the proper cure, ran flexing tests on those proper cures and the average results of the three laboratories showed flexing tests about 20 per cent better in the case of the Selenium stock than of the non-Selenium stock. More recently friction stripping tests at 0° and 100° have been made, and in Figure 10 there is shown the stripping friction strength of those two compounds at three temperatures. You will note that one compound without Selenium loses in friction strength as the temperature increases, and the other compound containing Selenium gains in friction stripping strength as the temperature increases. Both samples were made in a rubber factory.

It should be borne in mind that the flexing tests were made at room temperatures or possibly a few degrees higher, not at 100°

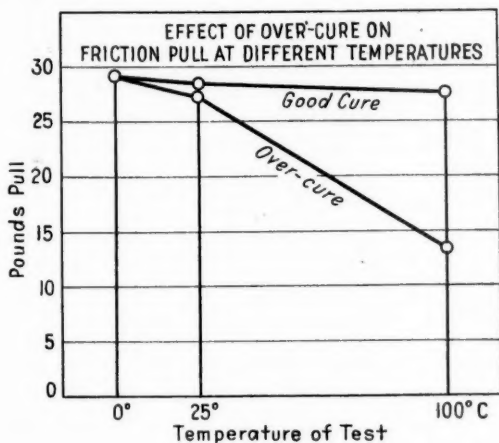


Fig. 8

where the advantage for Selenium is shown in the friction stripping tests. The compounds A and B following Figure 10 give the results shown in that graph.

Friction stripping tests at 0°, 25° and 100° have been made on another series of compounds mixed and cured in the form of belts by a second company, and that data is shown in Figure 11.

The compounds C and D following Figure 11 give the results shown in that graph, and the results obtained when tested on the flexing machine are also shown. Those flexing tests are made at room temperature. The temperature of the enclosed chamber in the testing machine is approximately 10° above room temperature. The actual temperature of the samples is not known.

Still another pair of compounds with and without Selenium made in the form of belt samples by a third company has been used in

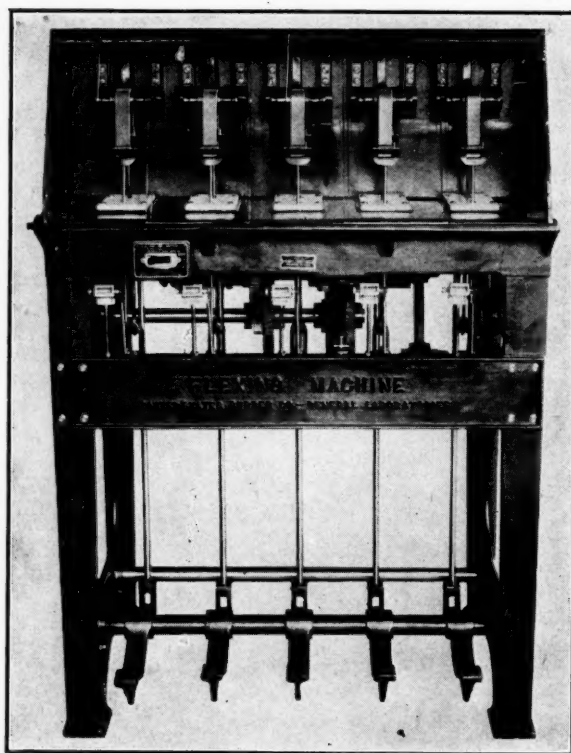


Fig. 9

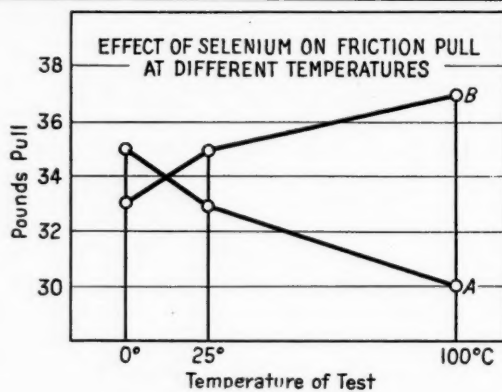
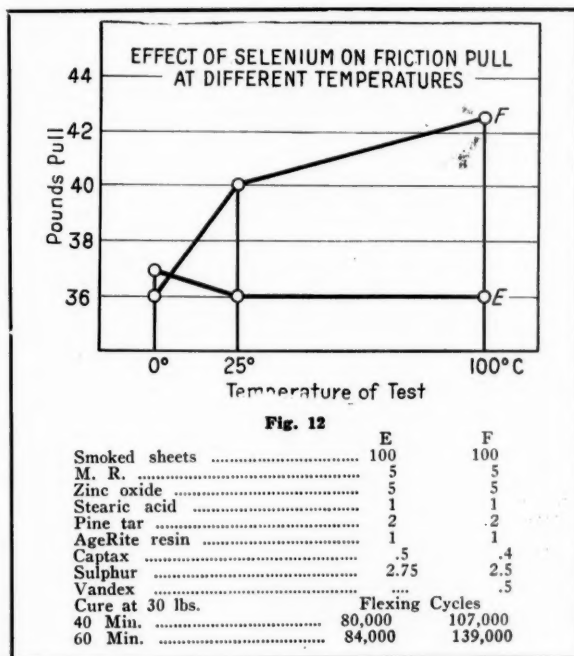
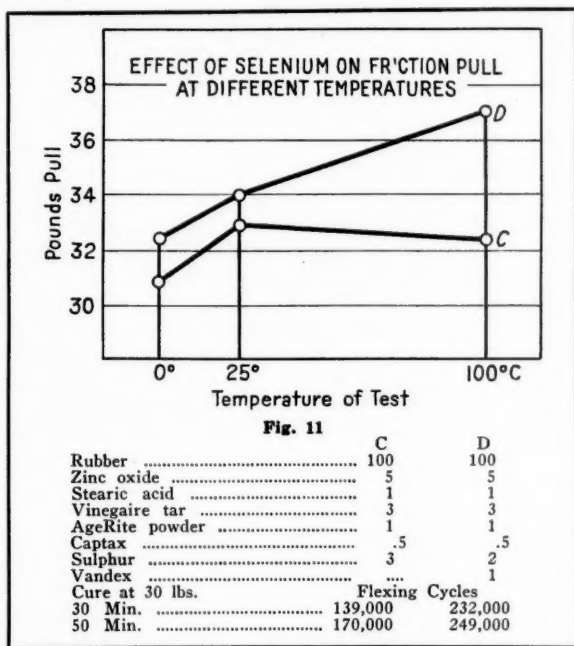


Fig. 10

	A	B
Rubber	100	100
M. R.	5	5
Zinc oxide	5	5
Stearic acid	1	1
Pine tar	2	2
AgeRite resin	1	1
Captax3	.3
Sulphur	3	3
Vandex5	.5



making the friction stripping tests at 0°, 25° and 100° C., and the data is shown in Figure 12. The two compounds in question, together with flexing data are given below the graph.

These same two compounds have been made up in the form of tire carcass stocks and are still undergoing tests.

While it would appear from the testing machine data that the addition of Vandex Selenium undoubtedly improves both the flexing and stripping qualities of friction stocks, it should also be borne in mind that the control stocks used are unusually high grade, giving unusually good flexing qualities, and that Selenium has improved those stocks that were already unusually high in quality. It has not been a case of using Selenium to improve what would otherwise have been a poor stock.

All of that work mentioned above has been solely laboratory work, and it may be said that laboratory machines do not always duplicate service conditions. It is a more simple matter to test small belts, such as an automobile fan belt. Automobile engineers have designed a machine for testing fan belts, and this machine duplicates actual service conditions, aside possibly from dust and

oil, so closely that the results obtained by the use of that testing machine should compare very closely with actual wearing tests on belts in actual service on automobiles.

The fan belt testing machine consists simply of an electric motor with four driving pulleys on the shaft which furnishes the power for operating four belts simultaneously. These four belts operate over four independently driven pulleys. The belts are under tension and the pulleys are the same size as those used on an automobile. The belts under test are driven at the same speed as a belt in service when an automobile is traveling at the rate of about twenty-five miles per hour. Accordingly, the life of a belt on this testing machine should be the same in hours as when the belt is used in actual service on the automobile. The machine is shown in Figure 13.

A company manufacturing fan belts has by means of this testing machine

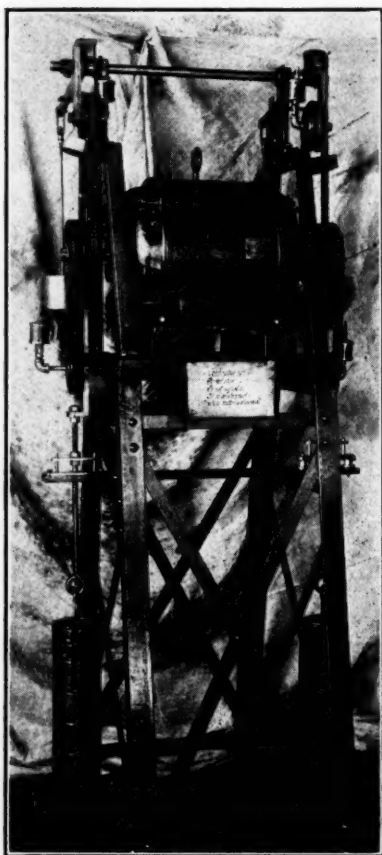


Fig. 13

greatly increased the life of its belts through improved compounding and construction methods so that the life of its fan belts on this testing machine has now reached about 800 hours or equivalent to 20,000 miles on an automobile. About three months ago they began to experiment with Selenium. Their first experiment was that of simply adding Selenium to what was already their best compound and shortening the time of cure. The first belt made with the addition of Selenium to the rubber compound has now run a total of 1,728 hours (which is the equivalent of about 43,000 miles) and was still running yesterday in good condition.

Discussion

Mr. BIERER (Chairman):

I think we will all agree that Somerville has again demonstrated that he knows how to talk and that we did not make any mistake in urging him to speak here today.

In confirmation of the figures which you have just been shown, let me say that just this last week at the Boston Woven Hose & Rubber Company we have completed an experiment wherein we reduced the sulphur slightly in one of our high grade belt friction compounds, added Selenium and the flexing tests obtained through that change were more than 100 per cent better than those given by the regular commercial stock.

Mr. MORSS (Simplex Wire & Cable Company):

Selenium will not vulcanize rubber without an accelerator. Therefore, rubber was not vulcanized with Selenium by Mr. Boggs until after he developed his accelerator in 1913. Our patent application was filed early in 1914 and resulted in two patents, one issued in 1917 and the other in 1920.

Rubber vulcanized without sulphur with Selenium and an accelerator showed much longer life than the same compound vulcanized with sulphur, but owing to the extra cost it was some years before we found a commercial application. In 1925 we improved the wearing qualities of our Tirex cable by vulcanizing the rubber with a mixture of Selenium and sulphur, and during the past three years our consumption of Selenium has averaged a little over 1,000 pounds per month.

It so happens that we are also interested in Selenium from quite a different standpoint; that is, its really marvelous properties as a flameproofing material. In the Fall of 1923 we had the problem of producing a wire covered with rubber and a cotton braid, which should not carry fire. We gave this problem to Arthur D. Little, Inc., and the actual work was done by Mr. Crocker of his staff, and they solved the problem by the use of Selenium and the process was covered by patent application in February, 1924.

At this time the market price of Selenium was about \$2.00 per pound and the 1924 production was only about 200,000 pounds, and the producers were selling it as fast as they could get it, largely for the production of red glass. There was apparently going to be so much difficulty in obtaining any considerable quantity of Selenium that in June, 1924, I asked the purchasing agent of the Western Electric Company of London to see if it could be obtained in Europe. He reported that he could buy it there at about \$2.25 per pound, but that it would be imported from this country.

After buying several small lots we tested out the possibility of obtaining a supply by ordering 300 pounds per week for eight weeks. As our expected demand for Selenium for flameproofing purposes did not materialize, we accumulated a little over 3,000 pounds by the end of 1924. For the moment this appeared to be something of a white elephant on our hands, but it came in very handy when we began to use Selenium for vulcanizing rubber the next year.

Having found that Selenium toughened the rubber on cable, it immediately occurred to us that it could be used to great advantage in tire treads, but if so used the demand would be greater than the supply. On the theory that a supply of any material can always somehow be found to meet a demand, we made a strong effort to find a source of supply for a considerable quantity. Not only did we write to possible suppliers all over the world, but we also advertised in the *Engineering and Mining Journal*. As a result, one man appeared who said he could produce 200 tons of Selenium additional per year, and as yet we have not been able to furnish him sufficient orders to satisfy him. A little later another responsible man claimed that he could produce 100 tons of Selenium per month, but so far we have not demonstrated whether or not he can make good because we have not been able to offer him a market.

While Selenium has never yet been produced in large quantities, it is my opinion that we shall find a way to supply the rubber manufacturers with all they may need.

Mr. GLIDDEN (Hood Rubber Company):

A little work has been done in the laboratory at the Hood Rubber Company by Mr. Reed under the direction of Mr. Glancy. In a typical tread compound 2 per cent on the rubber of Selenium was substituted for 1 per cent of sulphur. In other cases varying amounts of sulphur, Selenium and accelerator were used. In still another case we used rather high amounts of carbon black,

and substituted 45 per cent of the weight of sulphur with Selenium. Without going into details of the elongation, resilient energy, etc., the results can be summed up in a general statement that Selenium shortens the time of optimum, gives a somewhat higher tensile and considerable increase in hardness. The aging was slightly better than that obtained in the control compounds. This suggests the important point that greater production may be obtained from a given amount of equipment.

I do not know that any work has been done on inner tube stocks, but I think that a greater production of molded tubes might be obtained having less difficulty with their aging properties. The results that we obtained, while not comparable with those shown by Dr. Somerville, gave a hardening or stiffening effect in the rubber, and this may account in some degree for the improved life and adhesion obtained by him. Mr. Boggs and Mr. Follansbee, in a very interesting paper published in 1927, suggested that further work be done regarding the mechanics of sulphur and Selenium vulcanization.

The older men engaged in rubber work and those like myself, not educated as chemists, have always considered the melting point of sulphur as an important point around which to work. Selenium melts at comparatively high temperatures, 216° C. or 420° F, sulphur melts at between 230° and 240° F. It would be interesting if we could have some discussion on this phase of the subject.

MR. BIERER:

There is one company represented here that has done a great deal of work on Selenium in the manufacture of rubber belting.

MR. SCHILDHAUER (Manhattan Rubber Mfg. Co.):

During the past year we have been working with Dr. Somerville on Selenium in belt frictions. The results shown by Dr. Somerville are rather conservative since his control stock gives an unusually high flexing figure to begin with. As an example, the results of flexing tests made of the leading first grade transmission belts by a sub-committee of the A. S. T. M. Committee D-11 in making a study of the flexing machine, showed an average flexing of about 30,000.

In our own laboratory we have taken a friction stock, the flexings of which ranged from 30,000 to 85,000 at various cures, and by replacing part of the sulphur with Selenium we have increased the flexings to 150,000-200,000.

We believe that Selenium will be one of the most important compounding materials in the improvement of friction stocks in the next few years.

MR. BLAKE (Simplex Wire & Cable Company):

Last September Dr. Somerville showed that a test at 100° C. accentuated overcure. He has now shown that Selenium compounds withstand high temperatures very well. In other words, the implication is that compounds containing Selenium are not overcured, but that their elastic properties extend over a wide range of temperatures.

To appreciate this effect one should know how Selenium acts when used alone. Selenium melts at 217° C., which is above normal vulcanizing temperatures, and when rubber and Selenium are heated together at or above this melting point, nothing happens. If an organic accelerator is added, vulcanization takes place very much below the melting point of Selenium. Selenium is soluble in rubber to the extent of about 0.5 per cent at vulcanizing temperatures, which is one of the reasons why Selenium can act as a vulcanizing agent at temperatures far below its melting point.

All attempts to make hard rubber by using Selenium as the vulcanizing agent are absolute failures. No matter how much Selenium is used or how severe the cure given the mixture, one cannot get a product that at all resembles hard rubber. With sulphur the case is different, as both soft and hard rubber can be obtained. In other words, sulphur plays a double role in the vulcanization of rubber, while Selenium can play only one role.

Soft rubber and hard rubber are two distinct products. The intermediate product which varies from overcured soft rubber to semi-hard rubber ages very poorly, and in most rubber compounds it is desirable to avoid this intermediate stage in vulcanization. Furthermore, hard rubber is essentially a plastic substance quite sensitive to temperature changes, while properly cured soft rubber is essentially elastic and shows a minimum change in physical properties with temperature. This accounts for the results of tests at 0° C. and 100° C.

If the above statements are true, then it is not surprising that compounds vulcanized with a mixture of sulphur and Selenium, in which the sulphur is reduced below its over-curing point, should show abnormal properties. They can produce a soft vulcanized rubber which is completely cured without being overcured. That, I think, is the explanation of Dr. Somerville's results.

MR. GLANCY (Hood Rubber Company):

I would like to ask whether the Selenium bloom can be controlled.

DR. SOMERVILLE:

We know very well that if one is working with a compound containing sulphur and when given a certain cure it shows a sulphur bloom, as Selenium is added to the compound it is going to show a Selenium bloom, a green bloom instead of a gray bloom. We think that it is the sulphur bloom which comes out to the surface and brings with it the Selenium bloom. We think that ordinarily if the compound contains a rather low percentage of sulphur, say 2 per cent on the rubber, as much as 1 per cent of Selenium may be added without any Selenium bloom resulting, but I am not going to guarantee it.

A Comparison of the Rate of Combination of Sulfur with Rubber and the Rate of Vulcanization

E. R. Bridgwater

DYESTUFFS DEPT., E. I. DUPONT DE NEMOURS & CO., INC., WILMINGTON, DEL.

IT has been recognized for many years that accelerated compounds usually develop their maximum physical properties with a lower percentage of combined sulfur than is required for the correct vulcanization of an unaccelerated compound. It is furthermore well known that accelerators differ among themselves with respect to the degree of sulfur combination which accompanies a given degree of vulcanization. This has been attributed by some to the fact that accelerated compounds are exposed to less heat for shorter periods of time than unaccelerated ones. Others have suggested that accelerators may have a specific physical effect on the rubber which accounts in a large measure for the low combined sulfur required for vulcanization in the presence of some accelerators. The primary purpose of the tests described herein is to determine which of these effects is primarily responsible for the low combined sulfur at correct cure which characterizes highly accelerated stocks.

The rate of combination of sulfur with rubber is generally recognized not to be a measure of the rate of vulcanization. For the purposes of this discussion we will define vulcanization as a change in the physical state of the rubber which is accompanied by an increase in the tensile strength and stiffness of the product and by a decrease in the rate of swelling in hydrocarbon solvents. Other changes which take place on vulcanization are an increase in the elasticity and a decrease in the tackiness. These changes are also often used for the purpose of measuring the rate of cure or determining the correct cure but have not been considered in this study.

If the low combined sulfur required for correct cure of accelerated compounds were due wholly to the fact that accelerated compounds are vulcanized at lower temperatures for shorter periods of time and therefore subjected in a lesser degree to the deteriorating effect of heat, we would then expect that the combined sulfur at the correct cure or at comparable states of cure would be the same for all compounds having the same rate of cure, regardless of what

*Paper delivered at annual meeting of Rubber Division, A. C. S., at Swampscott, Mass., Sept. 10-15, 1928.

accelerator was used. The data shown in Table I prove that such is not the case. This table shows the stress-strain properties and combined sulfur for several different cures of four rubber compounds. The compounds are identical excepting that a different accelerator was used in each and the percentages of accelerator so proportioned as to give approximately the same rate of cure. The accelerators used were chosen to represent four distinct types of accelerator. The first is commercial Vulcanex which is typical of the aldehyde-amines resinified with formaldehyde. The second is commercial Vulcanol, a thiazine derivative. The third is mercaptobenzothiazole and the fourth methylene-para-toluidine which is representative of the simple Schiff's bases. The first three compounds have substantially identical rates of cure as judged by the stress-strain properties. The fourth is somewhat slower curing. The table also shows the percentage of combined sulfur to the rubber at each cure and the percentage of benzol that is absorbed during 15 minutes' immersion at 82°F. The benzol used was a standard commercial grade having the following distillation range:

F.D.	42.5°C.
5 cc.	52.0°C.
25 cc.	63.0°C.
50 cc.	74.5°C.
75 cc.	96.0°C.
85 cc.	106.0°C.
92 cc.	121.0°C. (dry)
Residue	2.5 cc.

Although the Vulcanex, Vulcanol and mercaptobenzothiazole compounds have identical rates of cure as judged by the stress-strain properties, the rate of combination of sulfur is not the same and neither is the benzol absorption. The rate of combination of sulfur with rubber is distinctly lower for the Vulcanol compound than for either the Vulcanex or mercaptobenzothiazole compound. On the other hand, the Vulcanol compound is stiffer at comparable cures than the mercaptobenzothiazole compound and absorbs benzol less readily. The Vulcanex compound is stiffer than either of the others and absorbs benzol still less readily than any of the three cures which were run. However, the rate of combination of sulfur with rubber is practically the same for the Vulcanex compound as for the mercaptobenzothiazole compound. These data clearly show that the time and temperature of cure are not the sole factors in determining the amount of combined sulfur required to produce any given state of physical cure.

The compound accelerated with methylene-para-toluidine cures more slowly than any of the others. The combined sulfur at the 90 minute cure is practically the same as the combined sulfur at the 45 minute cures of the Vulcanex and mercaptobenzothiazole compounds but they are less fully cured in 45 minutes than is the methylene-para-toluidine compound in 90 minutes. These tests indicate that there is no relationship between the combined sulfur required for a given state of cure and the activity of the accelerator. Such a relationship has often been said to exist, that is, rubber chemists have generalized that active accelerators or ultra-accelerators were in general low sulfur accelerators. Such does not seem to be the case. The combined sulfur required for correct cure also

TABLE I

Relationship Between Combined Sulfur and State of Cure														
		Accelerator	% Used	Cures	Combined Sulfur	Benzol Absorption	300%	400%	500%	600%	700%	800%	Tensile Strength	Ultimate Elongation
Formula	100.0	Vulcanex	0.875	20x140	1.32	69	150	250	450	925	1675	2800	2925	810
				45x140	2.38	61	225	375	675	1450	2625	3025	730
				90x140	3.28	60	250	450	850	1725	2900	690
Smoked Sheets	10.0	Vulcanol	0.375	20x140	0.95	74	100	150	275	575	1050	1875	2350	850
				45x140	2.00	64	175	350	575	1125	2225	3375	790
				90x140	2.82	62	225	400	700	1425	2600	2900	720
Zinc Oxide	1.0	Mercapto-benzothiazole	0.375	20x140	1.19	73	150	175	275	475	950	1700	2350	870
				45x140	2.32	70	175	250	400	750	1425	2575	2575	800
				90x140	3.30	69	175	300	500	850	1575	2525	780
Sulfur Accelerator	4.0	Methylene-para-toluidine	2.0	45x140	1.20	66	125	175	500	600	1175	2050	2400	830
				90x140	2.34	61	225	425	775	1675	3100	3225	710

TABLE II

Relationship Between Combined Sulfur and State of Cure													
	Accelerator	% Used	Cures	Combined Sulfur	Benzol Absorption	300%	400%	500%	600%	700%	800%	Tensile Strength	Ultimate Elongation
Formula<													

* Indicates best cure, as judged by tear, tack and snappiness.

appears to have no relationship to the modulus characteristics of the accelerator and is certainly unrelated to the benzol absorption because the one of these four accelerators which requires the least combined sulfur for correct cure, namely Vulcanol, produces compounds which swell in benzol as little as any.

Percentage of Accelerator Doubled in Table II

Table II shows the results of similar tests on three compounds which are identical with the first three shown in Table I excepting that the percentage of accelerator is doubled in each case. The fourth compound in Table II is accelerated with tetramethylthiurammonosulfide, the percentage being such as to give the same rate of cure as that of the other three compounds. These compounds were cured at 130°C., whereas those in Table I were cured at 140°C. We again find that Vulcanex and Vulcanol produce compounds having the same benzol absorption at comparable cures but that the mercaptobenzothiazole and tetramethylthiurammonosulfide compounds have distinctly higher benzol absorption values at equivalent cures. Equivalent cures is here used as meaning cures having similar stress-strain properties. These tests also check those in Table I in that the Vulcanol compound has lower combined sulfur at comparable cures than any of the others. It is worthy of note that the most powerful of these four accelerators, tetramethylthiurammonosulfide, is not the one that produces the lowest combined sulfur at the correct cure, again emphasizing the fact that there is no relationship between the activity of an accelerator and the combined sulfur at correct cure. There is also no direct relationship between the modulus characteristics of the accelerator, the combined sulfur and the benzol absorption.

The tests shown in Table III illustrate the effect of the percentage of accelerator used on the percentage of combined sulfur required to produce any given state of physical cure. The same accelerator was used in all of the compounds. The first compound containing 0.375% of accelerator is correctly cured in 60 minutes at 140°C. The second compound contains $2\frac{1}{3}$ times as much accelerator and is correctly cured in $\frac{1}{3}$ the time required for the less highly accelerated compound. The stress-strain properties of the 20 minute cure for the compound containing 0.875% of accelerator and of the 60 minute cure for the compound containing 0.375% of accelerator are identical but the more highly accelerated compound has a much lower combined sulfur. The third compound contains twice as much accelerator as the second. The 60 minute cure at 130°C. has the same stress-strain curve as the 90 minute cure at 140°C. of the compound containing half as much accelerator but again the combined sulfur of the more highly accelerated compound is lower. Comparing the data in this Table with Tables I and II it appears that the percentage of accelerator has a greater influence upon the combined sulfur required for correct cure than the nature of the accelerator used.

Effect of Percentage of Sulfur

The data shown in Table III give no indication as to whether the lower combined sulfur for the more highly accelerated compounds is due to the stiffening or polymerizing action of the accelerator or merely to the lesser deteriorating effect of heat. Table IV, however, shows the effect of increasing the rate of cure by in-

TABLE III

Combined Sulfur vs. State of Cure (Varying Amounts of Accelerator)												
Formula	Combined Sulfur	% Vulcanex	Cures	Combined Benzol Sulfur Absorption	Stress at Elongations of					Tensile Strength	Ultimate Elongation	
					300%	400%	500%	600%	700%	800%		
Smoked Sheets	100.0	0.375	60x140	1.74	69	175	250	400	775	1550	2750	810
Zinc Oxide	10.0	0.875	20x140	1.32	69	150	250	450	925	1675	2800	2925
Stearic Acid	1.0		45x140	2.38	61	225	375	675	1450	2625		3025
Sulfur	4.0		90x140	3.28	60	250	450	850	1725			2900
Vulcanex	As Noted	1.75	30x130	1.67	56	175	275	550	1150	2100		3250
			60x130	2.47	52	225	425	825	1775	3150		3725

TABLE IV

Combined Sulfur vs. State of Cure (Varying Amounts of Sulfur)												
Formula	% Sulfur	Cures	Combined Sulfur Absorption	Stress at Elongations of					Tensile Strength	Ultimate Elongation		
				300%	400%	500%	600%	700%			800%	
Smoked Sheets	2.0	30x130	0.70	74	100	175	325	650	1225	2175	2400	825
Zinc Oxide		45x130	0.97	73	175	285	425	825	1625	2800	3075	820
Stearic Acid		90x130	1.21	68	200	300	550	1125	2125	2900	3000	755
Vulcanex	4.0	20x130	1.17	67	150	225	400	725	1375	2400	2600	815
Sulfur	8.0	30x130	1.67	66	175	275	550	1150	2100	3250	3250	780
		10x130	0.76	59	150	225	400	750	1375	2300	2475	820
As Noted		20x130	1.50	54	175	350	575	1175	2150	3400	3400	790

creasing the percentage of total sulfur making no change in the percentage of accelerator or in the other ingredients of the compound. The curing temperature is the same for all three stocks, 130°C. There is little difference between the combined sulfur of the compound containing 4% of sulfur cured 20 at 130 and of the compound containing 2% of sulfur cured 45 at 130. These compounds have approximately the same rate of cure. The compound containing 8% of sulfur cured 10 at 130 also has about the same rate of cure but has distinctly lower combined sulfur. The compound containing 8% of sulfur cured 20 at 130 is slightly more fully cured than the compound containing 4% of sulfur cured 30 at 130. However, in spite of the fact that it is more fully cured, the combined sulfur is distinctly lower. The benzol absorption progressively decreases as the rate of cure is increased by increasing the percentage of total sulfur. Compare the benzol absorption of the 45 minute cure on the compound containing 2% of sulfur, the 20 minute cure containing 4% of sulfur and the 10 minute cure on the compound containing 8% of sulfur. These are equivalent cures but the benzol absorption decreases as the rate of cure increases.

If we assume that the only effect of increasing the percentage of total sulfur is to increase the rate of cure due to the mass-action effect of the accelerator, we may then definitely state that the low combined sulfur at correct cure of accelerated compounds is due in part to the shorter time and lower temperature that is required for cure. This conclusion follows from the fact that the faster curing compounds in Table IV had lower combined sulfur at comparable cures than the slower curing compounds although the percentage of accelerator was the same throughout.

Summary:

The following general conclusions can be drawn from these experiments:

- 1—The low combined sulfur at correct cure which is, in general, characteristic of fast curing compounds is due both to the stiffening or polymerizing action of the accelerator and to the fact that fast curing compounds suffer less heat degradation during the cure. Some accelerators have a greater physical stiffening or polymerizing effect than others, that being the only way one can account for the difference in the rate of sulfur combination between Vulcanol and mercapto-benzothiazole, since Vulcanol which causes the combination of sulfur at a lower rate causes physical vulcanization or stiffening of the rubber at a higher rate.
- 2—The differences in the combined sulfur required to produce correct cure between one accelerator and another are not large as compared to the differences which result from changing the percentage of any given accelerator.
- 3—Accelerators differ among themselves in the benzol absorption which they impart to compounds. Neither the stress-strain curve nor the combined sulfur gives any information as to what the benzol absorption may be. The benzol absorption at any given state of physical cure depends even more upon the rate of cure of the compound than upon the accelerator used. In general, the higher the percentage of accelerator the lower is the benzol absorption. The effect

of high sulfur is apparently due to the rate of cure and not to the sulfur itself because the high sulfur compounds which swell relatively little in benzol have low combined sulfur. It is indicated that oil resisting stocks should be highly accelerated but not overcured. In no case has curing beyond the point of maximum stiffness of the stress-strain curve caused a decrease in the benzol absorption. Referring to Table I, there is but little difference between the benzol absorption between 90 and 45 minute cures of either of the first three stocks. To state it another way, benzol absorption depends nearly as much upon the rate of cure as upon the state of cure. These facts should be borne in mind in compounding oil resisting stocks.

The Mechanism of the Reinforcement of Rubber by Pigments*

Harlan A. Depew

THE NEW JERSEY ZINC COMPANY, PALMERTON, PA.

Dispersed pigment reinforces by increasing the tear resistance. Flocculated pigment hardens rubber and reinforces by increasing the resistance to cutting. It may also increase the tear resistance, but not to as great an extent as if the pigment were well wet.

The mechanism of the reinforcement by increasing tear resistance is that the pigment particles act as obstacles that cause the tear to proceed in a longer path going around the particles. Due to the round-about path, the component of the force in the direction of the tear may be small. Accordingly, it is possible in the case of a fine pigment to increase the tear resistance even though the rubber-pigment bond is much weaker than the rubber itself.

The hardness of a stock containing flocculated pigment is due to the rigidity of the structure assumed by the flocculated pigment.

During the early moments of hot vulcanization, rubber is semi-fluid and the degree of dispersion may be largely determined during this period; some of the pigments becoming dispersed and some becoming flocculated.

Flocculated pigment and large particles introduce uneven stresses during the straining of rubber that lower the reinforcement below what might be expected.

ABRASION resistance is one measure of the reinforcing power of a pigment in rubber. In a recent paper¹ it was shown that this reinforcement was the resultant of resistance to cutting due to hardness and of resistance to tear. That paper did not discuss how pigments gave tear resistance and hardness to rubber and this paper considers that side of the problem and pre-

(*) Paper presented at meeting of Rubber Division, A. C. S., Swampscott, Mass., Sept. 11-13, 1928.

¹Depew—Proceedings of the A. S. T. M. for 1928.

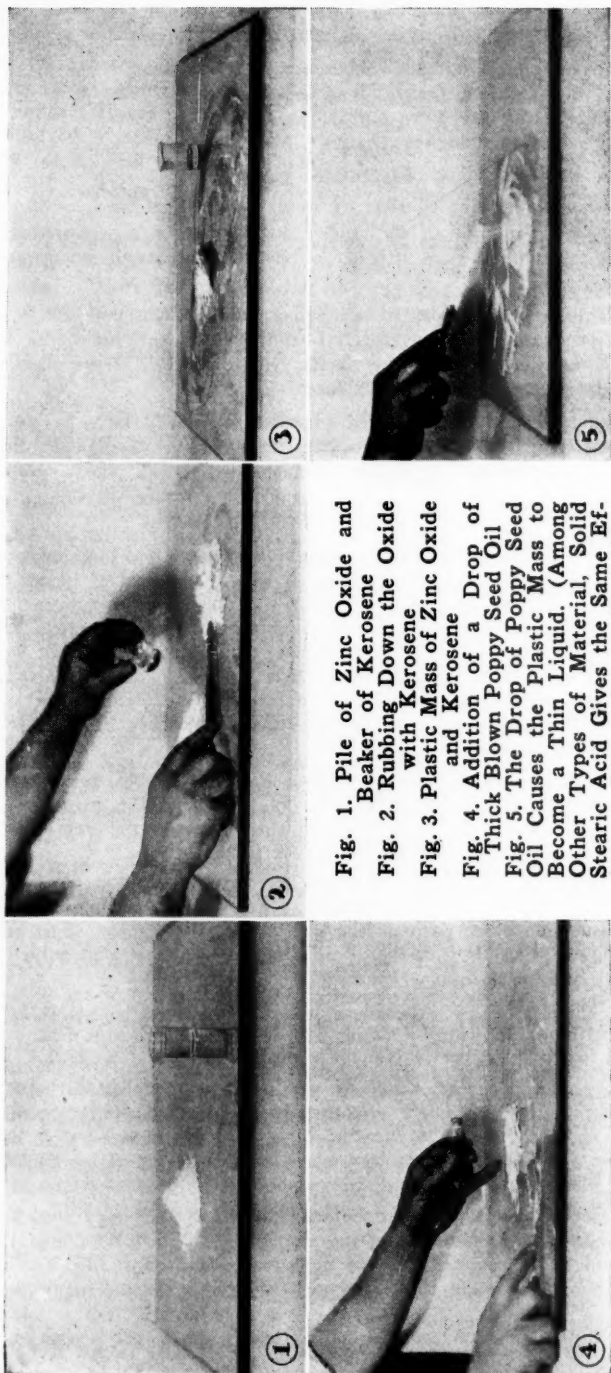


Fig. 1. Pile of Zinc Oxide and Beaker of Kerosene

Fig. 2. Rubbing Down the Oxide with Kerosene

Fig. 3. Plastic Mass of Zinc Oxide and Kerosene

Fig. 4. Addition of a Drop of Thick Blown Poppy Seed Oil

Fig. 5. The Drop of Poppy Seed Oil Causes the Plastic Mass to Become a Thin Liquid. (Among Other Types of Material, Solid Stearic Acid Gives the Same Effect as Blown Poppy Seed Oil.)

sents the idea that flocculated pigment is responsible for hardening a stock and that a dispersed pigment gives tear resistance.

Pigments may exist in rubber as:

1. Unmixed soft pellets
2. Agglomerates
3. Dispersed particles
4. Flocculated particles

Unmixed pigment consists of small pellets that have been carried into the interior of the rubber during mixing as a group and which roll around in a little pocket in the rubber and incorporate very slowly.

Agglomerates consist of a number of particles that are held together by a cementing material so that they will not break up during mixing in rubber or during vulcanization. They may be considered as large individual particles.

Unmixed and agglomerated pigments obviously have no reinforcing value in rubber. They cause weakness similar to that caused by porosity. It should be mentioned that a poorly wetted pigment may mix poorly and consequently a larger percentage of it is likely to be unmixed than if it be well wetted.

It is unusual to find large amounts of unmixed and agglomerated pigment in rubber. If the pigment is wet by the rubber, it will be pretty evenly distributed throughout the mass of the rubber and will be found dispersed to such an extent that every particle will be separated from every other particle. If the pigment is not well wet by the rubber, and if the particle size is small, the particles will be somewhat flocculated instead of being completely dispersed, for in the absence of wetting, the forces of flocculation tend to exceed the force of dispersion.

This paper is intended to present the idea, as has been stated, that flocculated pigment reinforces by increasing the hardness of the stock and that dispersed pigment increases the reinforcing properties by increasing the resistance to tear.

Taking up flocculation first, the method by which it hardens a rubber compound is analogous to the stiffness shown by the kerosene-zinc oxide paste in the well known experiment, illustrated in Figures Nos. 1 to 5, that F. P. Ingalls² demonstrated privately nearly ten years ago.

(NOTE: This experiment was demonstrated before the Rubber Division by Frank Breyer at the Pittsburgh meeting of the American Chemical Society in the Fall of 1922.)

In this experiment, a pile of zinc oxide was rubbed down with kerosene until it became a smooth plastic mass that could be molded into various shapes. A drop of highly viscous blown poppy seed oil or a small flake of solid stearic acid was rubbed in, and the once plastic mass thinned down and became as fluid as water.

Microscopic examination before and after the poppy seed oil³ had been added showed that the zinc oxide in the plastic material was highly flocculated; the particles were in groups, like bunches of grapes (to quote F. G. Breyer) whereas after the poppy seed

²John W. Masury & Son.

³Journal of Industrial & Engineering Chemistry, Volume 15, No. 2, P. 122 (February, 1923).

oil had been added each particle was separate and in Brownian motion.

Whether a pigment exists in a flocculated condition or in Brownian motion depends on the degree that the pigment is wet by the vehicle. If the pigment is sufficiently well wet there will be no flocculation and the individual particles will be seen to be dancing across the field of the microscope.

Coarse pigments are not seriously flocculated in rubber due to the relatively small flocculating force. As the particle size of a pigment becomes less, the tendency to flocculate increases; the amount depending on the degree that the pigment is wet by the rubber. If the fine particle sizes of a pigment stiffen a "compound," the material is poorly wet and the pigment is flocculated. If they do not harden it, the pigment is dispersed and the material of which it is composed is easily wet. Zinc oxide is an example of a material that is wet relatively better by rubber than most other materials.

The poor wetting of most materials by rubber is shown by the fact that in the finely divided form they tend to stiffen the rubber in which they are compounded. Microscopic observation shows the flocculation. It gives a hazy mottled appearance to a micro-section. The opaque spots frequently seen are unmixed pigment or agglomerates rather than flocculated pigment.

Since most of the fine size pigments reinforce rubber and make hard stocks, and since hardness has been shown to be a factor in reinforcement, it is reasonable to conclude that flocculation is responsible, at least in part, for the reinforcing properties of a poorly wet pigment.

A hardening effect in rubber, the same as caused by flocculation, occurs whenever a number of pigment particles get as close together as they do through flocculation, irrespective of how they come to be so close together. It may be actual flocculation, it may be heavy pigment loading, it may be some condition of mixing, or it may be a combination of these possibilities.

The mechanism of hardening due to flocculation is well recognized from the work on yield value of paints³. The "rough structure" developed by the flocculates resists deformation, due to the "frictional" forces developed when the pigment particles are forced to rub over one another during stressing.

For the second phase of the problem which consists in explaining how pigments give tear resistance to rubber, refer to zinc oxide. It is to be expected this pigment would be relatively well wet when we consider the chemical reactivity between it and the organic acids in the rubber, and it is proven by microscopic observation and through the data in Figure No. 6 that brings out the well known fact that the hardness of vulcanized zinc oxide stocks containing a fine pigment with a particle size of 0.15 of a micron is not greatly different from that of stocks containing zinc oxide with a particle size of 0.3 of a micron. Zinc oxide must be remarkably well wet by rubber for no flocculation to show up over this large range of particle size.

The question may arise as to why zinc oxide is not in Brownian motion in the rubber if it is well wet and the answer is that at room temperature, the rubber is too viscous for this to occur.

At ordinary vulcanizing temperatures (40 pounds steam—

141½°C.), however, there is a moment in the early part of the heat treatment when the rubber may be very fluid and it is during this moment that some of the poorly mixed pigment becomes better wet and more perfectly distributed. If dispersed the pigment is in Brownian movement at this moment and if poorly wet it becomes flocculated; the organic acid in the rubber playing an important part in bringing about the degree of wetting of reactive pigments.

The wetting of pigment by rubber will change during milling, during vulcanization, and during cooling as the interfacial tension of the rubber and pigment changes. The pigments are probably all less wet in vulcanized rubber than they were when the rubber was more fluid during the early stages of vulcanization.

Schippel⁴ has demonstrated the relatively superior wetting of zinc oxide by vulcanized rubber through the experiments in which he showed that the force of adhesion between rubber and zinc oxide was greater than that between rubber and any of the other pigments that he investigated.

The curves in Figure No. 6 show that the abrasion resistance and the tear resistance (Goodrich test using peanut shaped test piece) given by zinc oxide increase rapidly with decreasing particle size. (The tensile strength increases similarly but to a less degree.) Since reinforcement is the resultant of cutting and tearing resistance and since a well dispersed pigment does not increase the hardness or cutting resistance, it follows that the effect of a well dispersed pigment in rubber must be to increase the tear resistance of the stock.

The increased tear resistance given to rubber by well dispersed pigment may be explained by assuming that the particles are obstacles in the path of the tear and that they prevent a straight tear. The tear has to travel a much longer distance in going around the particles, and the change in the direction of the tear will frequently be such that the component of the tearing force in the direction of the tear will not be most effective. The "path of the tear" in rubber containing dispersed and flocculated pigment is visualized in Figures Nos. 7a and 7b.

(NOTE: Tensile tests are largely tearing tests but if the test piece is sufficiently small⁵, the test is a cohesion test and the tensile strength is very great.)

If the force of adhesion of the rubber to the pigment particle is greater than the cohesion of the rubber, the tear will proceed through the rubber going around the pigment at some distance and increase the tear resistance, whereas if the force between the pigment particle and the rubber is less, the tear will take place at the pigment surface and whether or not the pigment will lower or increase the resistance to tear will depend on whether the increase in length and change in direction of the tear is large enough to compensate for the lower force necessary to separate the rubber from the pigment.

It is quite possible that the bond between rubber and pigment is not sufficiently strong even in the case of zinc oxide to cause separation to take place through the rubber rather than at the interface.

⁴Journal of Industrial & Engineering Chemistry, Volume 12, No. 1, Page 33. January, 1920.

⁵Griffith Phil. Trans. Roy. Soc. London A-221, 163-98, (1920).

A pigment may give a considerable increase in tear resistance as well as in hardness, and it is probable, although not essential, that in this case only part of the particles are much better wet

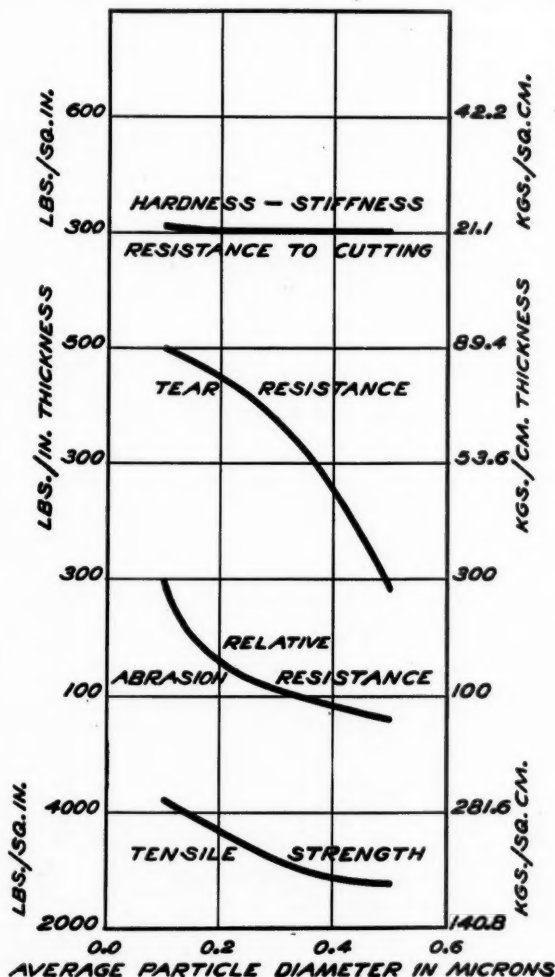


Figure 6
The Difference of Particle Size on the Rubber Making Properties of Zinc Oxide

than others and that the force of adhesion between the rubber and each particle will vary accordingly.

Green⁶ has enabled us to see this difference in wetting properties by microphotographs of stretched rubber containing barytes; the rubber has pulled away from some of the particles but not from

⁶Journal of Industrial & Engineering Chemistry, Volume 13, No. 11, Page 1029, November, 1921.

others (this is shown better in the original photograph than in the reproductions). The poorly wet particles of barytes are dispersed because the particle size is too large for flocculation to become a very great factor.

In the case of a fine pigment that is wet to a variable degree, part of the reinforcement will accordingly be in the nature of hardness and part will be tearing resistance.

Although flocculated pigment reinforces because it is flocculated, the reinforcement is of the hardness type and it frequently happens that the compounder wishes the pigment to reinforce by increasing the tearing resistance. It is easy to say, "Add a dispersing agent," but this is not easy to do. If we repeat the zinc oxide and kerosene experiment, substituting carbon black and kerosene we do not get dispersion on adding stearic acid or blown poppy seed oil. And in the case of rubber, we do not increase the dispersion by adding stearic acid and medium pine tar oil to a carbon black stock as shown by the curves in Figure No. 8.

(NOTE: Since the preparation of this paper, Goodwin⁷ and Park have published a paper in which they also report that neither stearic acid nor zinc stearate improve the dispersion of carbon black in petrol or rubber.)

The hardness of the black stock changes much the same with the addition of softener as the control stock without black and the tear resistance of the black stock, relative to the control, does not increase as it would if the softener had increased the force of adhesion between the black and the rubber. There may be materials that will wet carbon black in rubber better than the rubber itself, but stearic acid and medium pine tar oil failed.

(NOTE: The data given in Figure No. 8 were obtained from tests on the following tread compound approved by Sub-Committee XIV of D-11 of the A. S. T. M.)

Rubber (a)	1,000
D. O. T. G.	12½
Sulfur	35
XX Red Zinc Oxide	182
Carbon Black	400
Softener (b)	40-(0-160)

(a)—Pale Crepe and Smoked Sheet 50:50.

(b)—Double Pressed Stearic Acid and Medium Pine Tar Oil 50:50.

(400 parts of carbon black to 1,000 parts of rubber by weight calculates as 21 volumes of pigment to 100 volumes of rubber.)

A practical compounder will ask, "Then what does stearic acid do?" and he will point out that the gloss of a freshly cut carbon black stock increases as the stearic acid content increases and that the little pimples of unmixed pigment become less conspicuous. A number of these stocks have been examined carefully by microscopic methods with this thought in view, and it appears that the softer rubber compound has worked into the pimples of unmixed carbon black and broken them up into a number of smaller pimples that are less conspicuous. Possibly some of the unmixed black has actually become mixed, but it remains poorly wet and will be largely flocculated.

⁷Journal of Industrial & Engineering Chemistry, Volume 20, No. 6, Page 621 (June, 1928); No. 7, Page 766 (July, 1928).

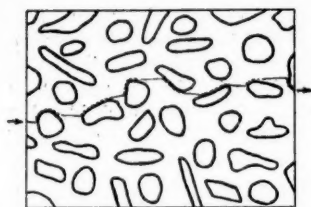


Fig. No. 7a

A two dimensional representation of the path of a tear through rubber containing dispersed pigment

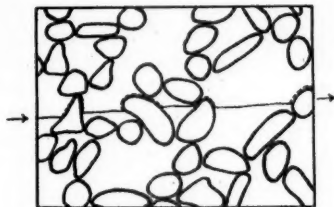


Fig. No. 7b

A two dimensional representation of the path of a tear through rubber containing flocculated pigment. The rubber separates easily from the pigment at the interface due to the poor wetting.

Note: Non-homogeneity of the rubber may cause the tear to become more irregular than shown above

Stearic acid may also improve the rubber compound by making the accelerators more effective through its chemical activity during vulcanization.

The opposite to starting with a flocculated pigment and dispersing it, is to start with a dispersed pigment and to add something that will flocculate it and thereby increase the hardness. A rubber

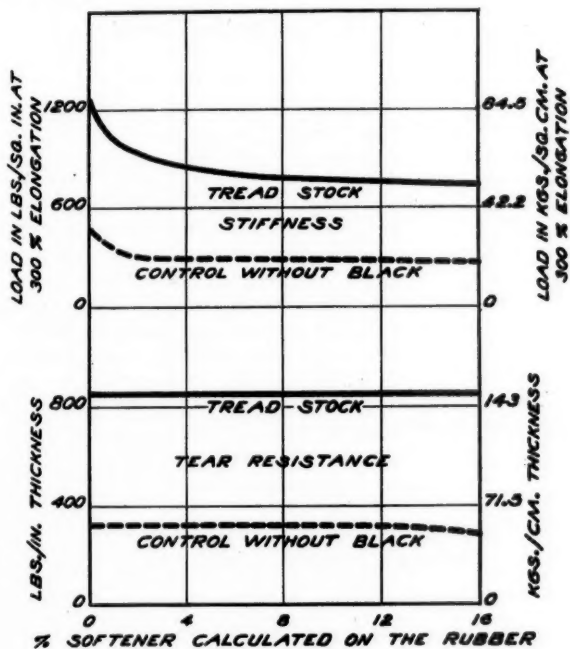


Figure 8

The Effect of Softeners on the Hardness and Tear Resistance of Tread Compound

stock containing zinc oxide can be hardened by the addition of hydrated lime which probably reacts with the organic acids present in the rubber and thereby removes them as effective dispersing agents. A lowered wetting can probably also be brought about by the addition of certain organic materials. It is probable that the degree of wetting of individual particles, first dispersed and then flocculated, will be very uniform.

At first thought one might conclude that much higher pigment loadings would be more practical than experiment has shown to be a fact since increased pigment concentration apparently increases both the hardness and the tear resistance up to the amount of pigment that can be mixed in the rubber. The trouble with this idea is that if a compound is too heavily loaded, the stresses will not be distributed evenly throughout the rubber and accordingly the unions at one pigment-rubber interface after another will have to carry too large a part of the stress and they will rapidly fail in sequence much the same as a rope fails when strand after strand breaks.

An attempt is being made to investigate the strains around pigment particles with a polarizing microscope.

It is practical to use much higher volume loadings with dispersed pigment than with flocculated pigment. This is the reason that a fine particle size zinc oxide (.15 microns) stock containing from fifty to sixty volumes of pigment to one hundred volume of rubber will give a greater area under the stress strain curve than any other commercial pigment, although it is not the smallest in particle size.

The non-uniformity in stress exists even around small pigment particles and is accentuated in the case of large particles, causing lower reinforcement than would be expected on the basis of the explanation given for the mechanism of pigment reinforcement if the condition of stress were neglected.

The mechanism of pigment reinforcement has been considered from the viewpoint of abrasion resistance in this paper but the idea could have been developed from a study of tensile tests. Flocculated pigment gives rigidity to rubber, stiffening the stress-strain curve, and dispersed pigment increases the length of the stress-strain curve since the tensile test is in part a tearing test.

At present many of the thoughts expressed are qualitative but as new and better testing methods are developed, they can be expressed in a more quantitative form. A better understanding of tear tests, of hardness tests, of pigment wetting, and of the distribution of stress in a rubber test piece will all be steps in the right direction.

[Reprinted from INDIA RUBBER WORLD, Vol. 79,
No. 5, pages 55-59. February, 1929]

Rubber As It Is Revealed by X-Rays

George L. Clark

PROFESSOR OF CHEMISTRY, UNIVERSITY OF ILLINOIS

THE beginning of the year of 1929 seems to be a logical time for considering critically the status of knowledge concerning the fundamental structure of rubber. Of all the contributions by various methods to the problem, those which have come as a result of the application of X-ray diffraction methods may be considered the most unique and perhaps most important in the past few years. It was known previous to 1925 that when rubber is strongly stretched it becomes warm, its specific gravity increases and it becomes doubly refracting. The name of J. R. Katz has become renowned throughout the world as a result of the experiment which he performed of causing a fine beam of X-rays to pass through a specimen of stretched rubber behind which was placed a photographic film. This experiment was one of those fortunate accidents which appear frequently in the history of science, but on the other hand, it was the result of clear thinking, rational deduction, and a keen appreciation of the possibilities of application of X-rays to the examination of the ultimate structure of materials.

The experiment had been frequently tried of attempting to deduce some information from the diffraction pattern of a single broad ill-defined halo obtained with unstretched rubber, but when this pattern was placed alongside one of rock salt or iron or calcite it was dismissed summarily as non-crystalline or "amorphous." After the discovery in 1913 by Von Laue and the Braggs, that crystalline materials serve as diffraction gratings for X-rays in the same way that finely ruled lines on glass will diffract visible light, a great number of materials were subjected to the method. Of course, single crystals or even fine powders of distinctly crystalline materials gave very definite patterns which were interpreted in terms of the ultimate architectural building scheme of these materials. Thus substances may be char-

acterized by a unit crystalline cell or primitive parallelepipedon of certain size in which the atoms or molecules are arranged in definite pattern; this imaginary unit subdivision of space with dimensions of a few hundred millionths of a centimeter and containing an integral number of atoms or molecules as usually designated in chemistry, has the properties of a visible crystal and actually produces this by indefinite multiplication of itself in all directions.

There is formed as a result, sets of parallel planes upon which the atoms and molecules lie, and which serve as a three-dimensional diffraction grating for X-rays simply because the interplanar distances are of the same order of magnitude as the wave lengths of X-rays. The logical consequences of fifteen years of X-ray fine structure studies have been an amazing growth of knowledge of the solid state of matter as might be expected from a powerful investigational tool which enables man to extend the powers of his vision, indirectly, far beyond the capacity of any

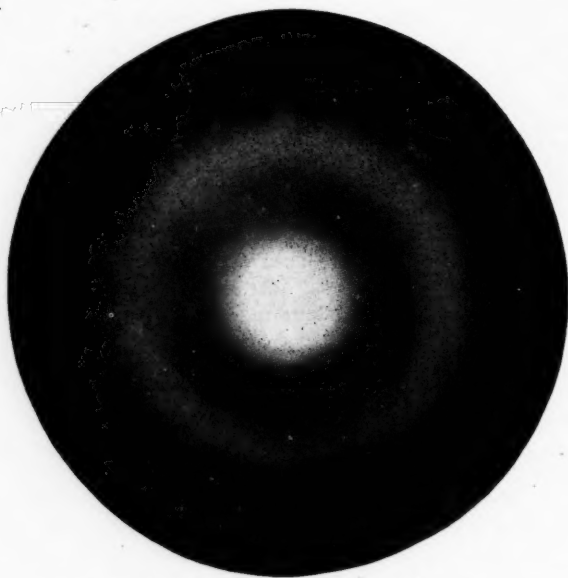


Fig. 1. Diffraction Pattern for Unstretched Rubber

supermicroscope. The method permits the deduction of the sizes and shapes of atoms and molecules and a knowledge of the orderly forces in crystalline materials. Because this information is genuinely fundamental the prevalent research effort is now to crystallize everything (instead of dissolving or melting solids). The chemist has now actually verified

the existence and measured the lengths of long carbon chains, and benzene rings and other compounds as well as six hundred or more inorganic compounds of every conceivable kind and complexity.

It is small wonder then, that great interest was aroused in 1925 by Katz' discovery that stretched raw rubber pro-

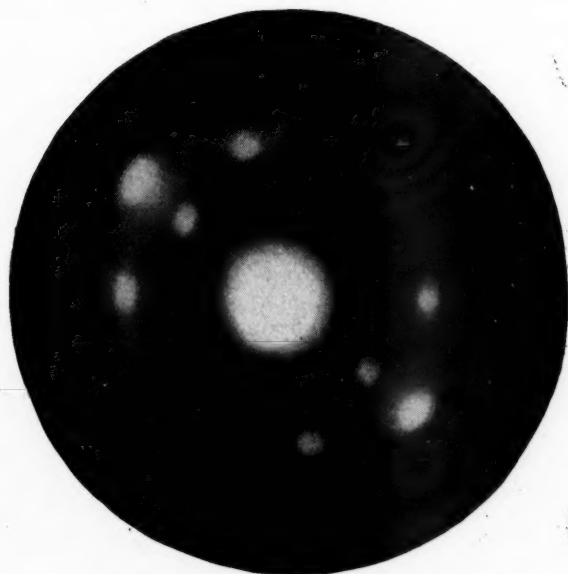


Fig. 2.—Diffraction Pattern for Raw Rubber
Stretched 500%

duces an X-ray diffraction pattern which seems to indicate crystallinity as clearly as does the pattern of an aluminum wire. For the ill-defined halo for the unstretched rubber, classed as the pattern of an amorphous substance, (Fig. 1) has given way to a pattern with definite interference points lying on various concentric circles and also on a series of hyperbolas (Fig. 2). With such a pattern it is possible by the straightforward methods of measurement and calculation to determine the ultimate structure of stretched rubber just as easily as that of crystalline aluminum drawn into a wire. In order to understand the real meaning of these results it is desirable to tabulate the essential experimental facts derived in the X-ray studies of rubber by Katz, Hauser and Mark, Feuchter, Meyer and Mark, the writer and others.

1. Kinds of Rubber. Natural rubber in practically every state, coagulated latex, crepe, smoked sheets, vulcanized sheets, etc., produce the fiber crystal diffraction pattern upon stretching. No synthetic rubber specimens thus far prepared have given more than the faintest evidence of the phenomenon

so that the fundamental process involved is a definite criterion of characteristic structure of natural rubber.

2. Elongation Required for First Appearance of Pattern. Raw rubber—above 75 per cent elongation. Vulcanized rubber—above 250 per cent.

3. Effect of Elongation on Intensity. Intensity of diffraction spots linearly increases with increasing elongation above critical value, while intensity of broad "amorphous" ring simultaneously decreases.

4. Positions of Interferences. Constant with increasing elongation.

5. Breadths of Interferences. Constant with increasing elongation, at least to 800 per cent; different in vulcanized samples as noted below; size of colloidal micelle may be calculated from breadths.

6. Effect of Method of Stretching. When stretched isothermally (very slowly) the interferences if appearing at all are very faint; when stretched adiabatically (very rapidly) maximum intensity of interferences at same elongation.

7. Time Required for Appearance of Pattern. Instantaneous upon stretching.

8. Effect of Temperature. Pattern disappears about 60° C.

9. Effect of Release of Tension. Process reversible and pattern disappears, though sometimes persisting for some time after release, particularly if specimen is cooled after stretching.

10. Effect of Solvent. Stretched specimens placed in solvent vapors no longer produce crystal pattern.

11. Racked Rubber. As a result of X-ray studies Feuchter has found it possible to extend rubber 10,000 per cent by successively stretching rapidly then heating until specimen contracts several times. The resultant thread gives a sharp X-ray pattern as detailed as with a pure organic compound; the racked rubber is insoluble and largely non-swelling in usual organic solvents (analogous to cellulose or silk fiber).

12. Effect of Purity. Purest extracted rubber, free from protein and resins gives a crystal pattern, providing that the phenomenon is associated with pure hydrocarbon C_6H_8 (polymerized).

13. Effect of Botanical Source of Latex. Appearance and positions of crystal interferences independent of botanical source. Balata and gutta percha are different from rubber and probably from each other.

14. Does Unstretched Rubber Ever Produce a Crystal Pattern? "Frozen" rubber (i. e. rubber which has stood for some time at low temperatures and has become opaque and hard) gives a pattern of sharp concentric rings indicative of small crystal grains in random orientation. These rings are spaced so that the interferences of stretched rubber fall

exactly on them. Frozen rubber may be distinguished from oxidized rubber by the fact that upon warming or several stretchings it becomes normal and the crystal pattern disappears leaving only the broad "amorphous" rings.

15. Effect of Fillers. The typical rubber patterns appear and in addition those characteristic of the crystalline filler (zinc oxide, carbon black, pigments, etc.). Upon stretching the most of the filler particles remain in random arrangement. (Exceptions, magnesium carbonate and sulphur as noted below.)

16. Effect of Calendering. Introduces a fibrous structure (lining up of units) which is indicated by the X-ray pattern even without stretching.

17. Effect of Mastication. Tends to destroy crystalline orientation even when the specimen is strongly stretched.

18. Synthetic Rubber. All synthetic polymerized rubber-like substances such as polymerized isoprene, metastyrol, butadiene, polyvinyl acetate, etc., produce an "amorphous" pattern similar to that of rubber which is retained unchanged up to the highest elongations. Katz¹, however, maintains that with a pure methyl rubber two crystal interferences (only) appeared in addition to the amorphous rings. Hock and Barth² with a precision camera have demonstrated also a distinct change during stretching of synthetic rubber at low temperatures in agreement with earlier predictions from the Joule effect. Metastyrol when stretched produces a pattern in which the amorphous ring splits into two segments in the direction perpendicular to the direction of stretching, very similar to the action of gelatine upon stretching, so that arrangement is taking place in one or two, but not in three dimensions.

19. Dimensions Calculated from "Amorphous" Pattern of Unstretched Rubber. Two broad rings are produced corresponding to the spacings 14.88 (inner ring) and 6.05 A. U. Experiments by the writer³ with very pure extracted rubber hydrocarbon very carefully freed from solvent give the values 11.15 and 5.97 A. U. In the presence of solvent vapor (swelling the rubber) the former value may increase up to 14.76 A. U. as a maximum. The inner ring is characteristic of polymerized substances, the outer one being found for corresponding pure unpolymerized liquids such as isoprene.

20. The Unit of Structure in Stretched Rubber. From the crystal fiber diffraction pattern obtained with stretched rubber it is possible to deduce crystallographic system, the size of the unit cell, and from this and the density the number of molecules of C_5H_8 associated with the ultimate architectural unit.

¹ *Chem. Zeitung* 51, 53 (1927).

² *Z. Physik. Chem.* 134, 271 (1928).

³ *Nature* 120, 119 (1927).

Inasmuch as the pattern for stretched rubber is a characteristic of a fiber, i. e. a large number of small crystal grains definitely alined, it is possible to derive the identity period along the axis of fibering or the direction of stretching by direct measurement and without any recourse to knowledge of the crystallographic space group. This is done by drawing hyperbolas through the diffraction spots (Fig. 2) and measuring the distance of the vertex of each hyperbola from the zero equatorial line passing through the center of the diagram. When the X-ray beam is perpendicular to the fiber axis, a is the specimen to plate distance, and e the distance on the photographic plate from the trace of the center to the vertex of the hyperbola, the relation $e = a \tan \mu$ can be used to obtain the angle of the diffracted beam from the primary beam. The identity period or spacing which repeats itself along the axis is derived from $I = n\lambda / \sin \mu$ where n is a whole number and λ the wave length of X-rays used. The other two dimensions of the unit cell are somewhat less readily determined from the position of the spots on the concentric rings which may be drawn through them. The following results have been obtained in these evaluations.

Authority	System	Dimensions			No. C ₆ H ₈
		a	b	c (fiber axis)	Groups per unit volume
Pummerer + Koch ⁴ (crystals)	Monoclinic	4.83	4.71	5.33	1
			$\beta = 77^\circ 19'$		
Ott ⁵	Cubic?	6.37			6 (atomic radii)
Katz ⁶	Orthorhombic	6.5	6.5	8.0	2 (density)
Hauser + Mark ⁷	Orthorhombic	8.0	8.6	7.68	3
Meyer + Mark ⁸	Rhombic	12.3	8.3	8.1	4 (possibly 8)
					8

In more than 75 precision measurements the writer has obtained as the average value of c , 8.003 Å. U. confirming the value of Meyer and Mark 8.1 ± 0.1 . The two other dimensions are also confirmed so it may be concluded that all other values are incorrect. Thus 8 isoprene groups—

CH₃
|
CH₂—C=CH—CH₂—

are grouped together as the unit of structure of stretched rubber. The value 8 (N) is derived from the expression

$$N = \frac{\rho \times 1.008 \times V}{Mm}$$

where ρ is the density (about 1.0 for the crystalline portion of stretched rubber), V is the volume of the unit cell, M

⁴ Ann. 438, 294 (1924).

⁵ Naturwissenschaften 14, 320 (1926).

⁶ Chem. Zeit. 49, 353 (1925).

⁷ Kolloid chem. Beihefte 22, 63 (1926).

⁸ Berichte 61, 1939 (1928).

is the molecular weight of the simple kinetic molecule C_5H_8 , and m is the absolute mass of the hydrogen atom.

21. The Sizes of Colloidal Micelles of Rubber. From the measurement of half-breadths of the X-ray diffraction spots, the size of the particles composed of the foregoing unit cells may be ascertained. Hauser and Mark first estimated the colloidal particle, which is that which ordinarily manifests itself, to contain about 4,000 C_5H_8 groups. However, since their unit cell dimensions were erroneous and since far more accurate methods of calculation of sizes in various directions are now available,⁹ the following values represent more nearly the truth; length along fiber axis

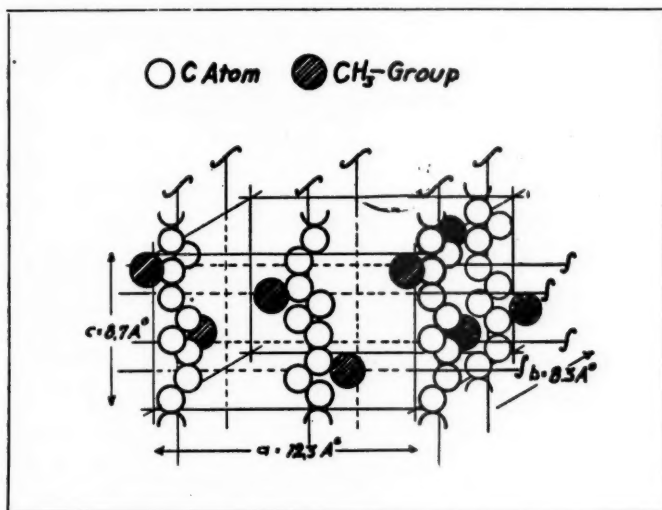


Fig. 3.—Elementary Unit of Rubber

300-600 A. U.; thickness 100-200 A. U. Hence the micelle contains 10,000-20,000 unit cells or 80,000-150,000 isoprene groups. The micelle appears to have the form of a long flat bundle.

22. Significance of the Very Small Unit of Structure of Rubber. The X-ray method has been subjected to bitter criticism by rubber, cellulose and protein chemists because the very small unit structural cell containing only 4 or 8 simple chemical molecules seems so incompatible with these substances of high molecular weight known to be polymers of simple parent molecules, even though the X-ray pattern in addition to the unit cell gives a measure of this colloidal micelle. The magnificent X-ray work of Hengstenberg in Staudinger's laboratory on the polyoxymethylenes, or polymerized compounds of formaldehyde,¹⁰ gives the key to

⁹ Laue, *Z. Kryst.* 64, 115 (1926); later papers by Patterson and by Brill.

¹⁰ *Zeit. physikal. chem.* 126, 425 (1927).

a seeming enigma.¹¹ Much of the difficulty lies in a confusion in terms, principally in the meaning of the word "molecule." Formaldehyde may form "endless" chains held together by primary valence forces just as is true in the simple molecule. Up to a length of about 45 formaldehyde groups, the X-rays will measure the *macromolecular* length. There is now incontrovertible evidence that isoprene groups form these "endless" chains in rubber, glucose residues in cellulose, and peptides in silk and other proteins. Hence unit cells do not contain the whole chains but only a sub-multiple. The space group for stretched rubber is V^4 , which means 3 two-fold screw axes. No complete rings or chains of 8 or 4 or 2 isoprene groups can possibly account for

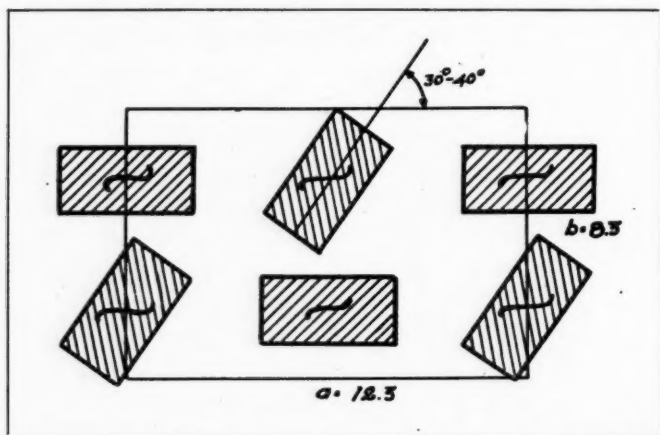


Fig. 4.—Elementary Unit of Rubber, Cross Section, Schematic, Through the Main Valence Chain and the Fiber Axis.

the experimental X-ray diffraction results. The structure proposed by Meyer and Mark which is undoubtedly correct, is shown in Figure 3. The primary valence chains lie parallel to the fiber axis and extend *beyond the unit cell throughout the whole colloidal crystalline particle*. In the cell itself 2 isoprene groups one above the other, account completely for the observed spacing, with one group turned at 180° to the other. The methyl groups are in *cis* position and the whole arrangement accounts for the screw axes which run through the crystal. The disposition is shown schematically in cross section Figure 4. Each rectangular section represents 2 superposed C_5H_8 groups; 2 belong wholly to the cell and the other 4 are shared by neighboring cell, giving a total of 8 isoprene groups per unit cell. How long are the long chains of C_5H_8 groups held together by primary valences? This length must be the same at least as the

¹¹ See the writer's paper "X-Ray Contributions to the Problem of Polymerization." *Ind. Eng. Chem.*, Feb., 1929.

measured size of the whole colloidal crystalline particle, 300-600 A. U., which means a chain of 75-150 isoprene groups as the "*structure-molecule of rubber*." These single long chains are not demonstrated in other properties such as osmotic pressure, but aggregates of them.

23. The Structure of Rubber. It is not the purpose here to consider critically all the theories of the structure of rubber which have been submitted to account chiefly for the property of elasticity, since this has been done recently.¹² The foregoing series of new experimental results leads to a comparatively simple structural picture based upon the long chains of isoprene groups lying side by side in parallel orientation along the direction of stretching. These are disoriented, though not necessarily completely resolved into the single chains, when the tension is released and the rubber no longer yields a crystal pattern. In the micelle these chains, possibly coiled in a spiral, are less compactly arranged as shown by a smaller density. The reversible labile condition and elasticity must be connected with the double bond. To saturate by hydrogenation or halogenation is to destroy the elastic properties. For a long chain in which appears a regular succession of double bonds would have a pronounced tendency to bend and to coil up as is amply demonstrated in calculations of molecular sizes from surface energy data for such acids as oleic as compared with saturated acids. Upon stretching these coils are straightened out into parallel orientation—thus is elasticity accounted for.

The other most recent theory, of Bary and Hauser, really reduces to the one just developed in the limit. The experiments of Freundlich and Hauser with the micromanipulator on latex particles, and fractionation experiments of Pummerer, Feuchter and others have produced convincing evidence of the presence of two hydrocarbons in rubber, a higher and insoluble polymer (β), and a lower soluble polymer α of the same basic molecule, namely C_5H_8 . If an insoluble β form is responsible for the crystal interferences, then α is dissolved in it to form a one-phase system. The ratio $n_1\alpha/n_2\beta$, where n_1 and n_2 are the numbers of the corresponding macromolecules,¹³ may be changed by temperature or mechanical treatment; n_1/n_2 is small at ordinary or low temperatures but increases with temperature or working. Upon "freezing" rubber β increases at the expense of α . Upon stretching α is squeezed out of β and these macromolecules in a sense crystallize or solidify and produce crystalline interferences. There is a clear similarity between rubber and liquid crystals. By the classical work of Friedel these are shown to be an intermediate mesomorphic state between amorphous and crystalline, namely

¹² Hauser, *Latex*, 1927. Bary and Hauser, *Kautschuk* 1928, 96.

¹³ This word is used to distinguish these large units or chains from the simple C_5H_8 molecule.

nematic, in which molecules are aligned in the same direction but not in equidistant layers, hence produce no X-ray diffraction effects. Lehmann and Vorländer's work on liquid crystals has demonstrated that these are formed only by long molecules in linear arrangement. However the tendency to form liquid crystals does not increase indefinitely with molecular length but reaches an optimum value. Thus while liquid crystals and racked rubber are in many respects analogous, they differ in that one diffracts X-ray like an amorphous liquid and the other as a sharply crystalline substance.

We are led once more to the conception of a preformed very long molecule formed by high polymerization of a simple hydrocarbon C_8H_8 in which the links, bound by primary valence forces, lie on screw axes,—and a small unit cell results. It is immaterial whether, in release from tension and return to the amorphous condition of rubber, these long molecules become coiled again, and out of parallel arrangement, or whether the two-phase system of β and α hydrocarbons again becomes a one-phase system with β swollen by α until the swinging amplitudes of the lattice points are too large for visible interference.¹⁴

One of the most eloquent analogies to this proposed structure of rubber is to be found in the recent X-ray studies of the system nitrocellulose-camphor (celluloid) by Ueda.¹⁵ As crystalline camphor is added and goes into solid solution in a nitrocellulose fiber, which alone gives a beautiful fiber diffraction pattern, this disappears and an amorphous ring is formed. Upon extraction of the camphor the nitrocellulose diagram is regained. If a celluloid film is stretched the camphor crystallizes out of solid solution and a nitrocellulose fiber diagram is formed. Substitute β and α rubber, respectively, for nitrocellulose and camphor and the phenomena are practically identical.

However the picture of spring-like long chains of isoprene groups which may be drawn into parallel orientation during stretching so that X-ray diffraction results as truly as from genuine crystals, is one of far greater simplicity and it explains adequately all the experimental facts enumerated in this paper. Evidences of more than one polymer are to be ascribed simply to micelles of different sizes, that is, long primary valence chains of different lengths or different numbers of chains bundled together in a micelle. The great stumbling block as to the significance of the very small unit of crystalline structure is entirely removed when it is understood that there are sub-periodicities along the chains, which

¹⁴ The general picture of the nematic state and of long chain molecules for rubber has been accepted by Katz, *Ergeb. exacter Naturwissenschaften* 4, 154 (1925); *Naturwissenschaften* 14, No. 38; and Fechter, *Kautschuk*, 1928, 103.

¹⁵ *Z. physik. Chem.* 133, 350 (1928).

are themselves as long as the colloidal particle itself, and that these small distances represent a turn in a screw axis. The great power of the X-ray method is proved by the fact that the same diffraction photograph gives both the chain length, or micellar size, and the comparatively tiny screw axis periodicity.

Here, furthermore, is provided a clear insight into the universal manner in which nature builds such materials as rubber, cellulose, silk, muscle fibers, chitin, etc. Stretched rubber is comprised of bundles of long chains the links of which are isoprene C_5H_8 groups; cellulose is analogous with dehydrated glucose residues $C_6H_{10}O_5$ as links; and the same is true of silk with polypeptide chains and of chitin with acetyl-glucosamine groups in chains. Thus do we have a universal architectural plan for vastly different building materials. While there are still many difficult and unsolved

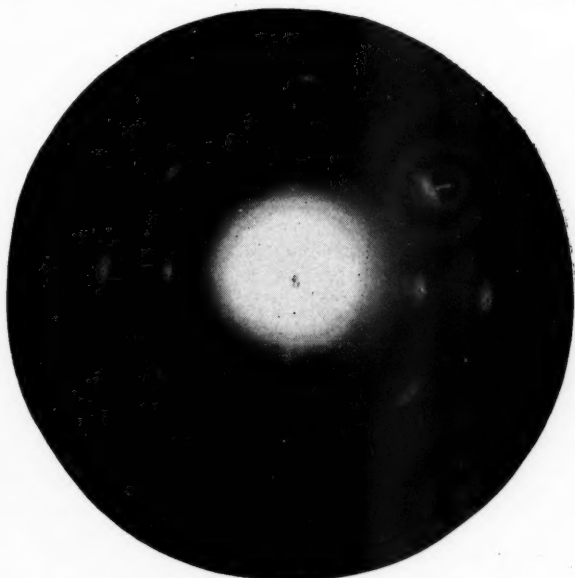


Fig. 5.—Diffraction Pattern for Vulcanized Rubber Stretched 500% (Note sharpness of spots as compared with Fig. 2).

details the X-ray method has simplified and rationalized one of the most difficult fields in chemistry and technology.

24. Some New Facts About Vulcanization. Meyer and Mark have shown the remarkable similarity between the reaction of sulphur chloride with ethylene (to form mustard gas) thus: $CH_2:CH_2 + SCl_2 = Cl.CH_2:CH_2)S$
 $CH_2:CH_2$ $Cl.CH_2:CH_2$

and with rubber, containing a hydrocarbon also of olefine

character and forming $(C_5H_8)_2SCl_2$. Thus in cold vulcanization bridges might be formed between double bonds in the same micelle and also between neighboring micelles (a micelle being a bundle of the long chains of isoprene groups as explained above). This results in the tying of micelles together at single points and ultimately in the formation of hard rubber without elasticity. One consequence at once is the tendency to form larger micellar units than those existent in raw rubber. This prediction is fully verified in new work by the writer. Careful measurements of diffraction interferences for stretched samples prove that the breadths are materially smaller than those for raw rubber (compare Figure 5 for vulcanized with Figure 2 for raw rubber) and hence that the colloidal particles are materially larger.

Furthermore numerous measurements on the positions of the hyperbolas of the fiber diagrams for stretched samples, in which the vertices have been accurately plotted from the equation of an hyperbola, indicate a small but distinct difference in the dimensions of the unit cell in the direction of stretching. The value for raw rubber is 8.003 A.U. while for the special vulcanized samples the value varies from 8.15 A.U. with very small amounts of sulphur down to 7.93 A.U. for large amounts. The contraction compares with that observed upon mercerization of cellulose. Patterns have been obtained in which excess small sulphur crystals very definitely fiber or orient themselves when the specimen is stretched. For the continuous diffraction rings for sulphur powder in random arrangement in the unstretched rubber change into symmetrical discontinuous arcs. This phenomenon has been observed heretofore only with magnesium carbonate filler. These new and unexpected results will be the subject of a later detailed paper.

The Evaluation of Carbon Blacks

D. F. Cranor and H. A. Braendle¹

THE present day application of carbon pigments to rubber compounding makes necessary a broader use of stress-strain data for the evaluation of individual blacks and classification of the members of this important group. A decade ago the rubber man's interest in pigments centered on their behavior in tire tread proportions, but now impingement process black is commonly used in loadings up to, and in some instances, above 100 parts by weight to 100 of new rubber, and the carbon family has grown through introduction of the materials commonly referred to as "soft blacks." Although performance tests, in particular aging and abrasion resistance, have been somewhat refined and further developed, stress-strain data remain the primary criteria and it is through employment of the newer conceptions developed from these that we can best draw a picture sufficiently complete to properly group and classify the various members.

Wiegand's paper, "The More Complete Evaluation of the Pigment Reinforcement of Rubber," gave to the industry in the "A" and "Delta A functions" more adequate measures of the effectiveness of pigments. The present authors have employed the "Delta A" criterion in the testing of carbon blacks; and since its derivation is fully covered in the original it is only necessary, before using this measure of rubber quality, to briefly discuss its significance.

The energy or proof resilience of a rubber compound undeniably combines more information regarding the quality of a given compound than does any other single criterion. Similarly for the comparison of pigments the "A" and "Delta A functions" sum up the stress-strain characteristics and indicate the limits of usefulness. The "A function" is the total energy which is developed by successively increasing pigment loadings in a chosen base compound, or in other words it is the integral of energy against compound loading. If we plot a curve giving the energy development by a series of pigment loadings (as in Figure 1), the shaded area, or the area under the curve, gives what may

NOTE.—Publication permitted by *Ind. & Eng. Chem.* Presented at the Swampscott meeting of the A. C. S., Sept. 10-14, 1928.

¹ Binney & Smith Co., New York, N. Y.

be called total energy, or the total stored work available from every type of compound which might use that pigment. Because this index has no strict physical counterpart it was necessary to invent a name and it was called the "A function." However, since the matter of greatest interest to the user of carbon black is the additional quality or extra toughness imparted by the pigment, the "Delta A function," which indicates this *extra* energy, is more generally useful. This is the integral of this excess energy with respect to loading, and is represented by the double-hatched area of Figure 2. Perhaps the "Delta A function" might best be described, however, as the energy capacity, or inherent energy, of a pigment in connection with a given base mixing.

Modulus

Modulus figures may serve as ready means for distinguishing between carbons of different sorts but must be employed most carefully to be at all significant. Recent researches have shown it necessary to determine very complete modulus data when such are to be used for evaluation of the carbon pigments, because, in

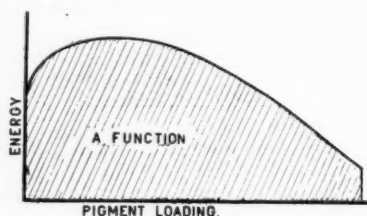


Fig. 1.

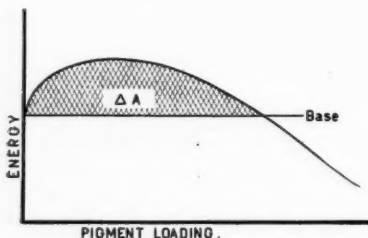


Fig. 2.

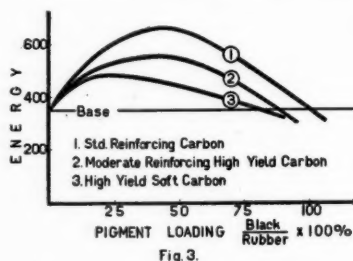


Fig. 3.

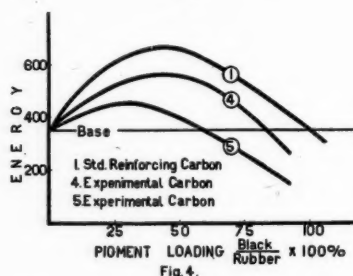


Fig. 4.

organically accelerated mixings, it is sometimes the case that although one black may yield a higher modulus than another if compared at 300 per cent elongation, the order becomes reversed if comparison is made at, for example, an elongation of 50 per cent. The data of Goodwin and Parks establish this point, which is fully substantiated by unpublished figures accumulated by the present writers.

This reversal of order is, however, profoundly affected by the

type of acceleration employed and it is still difficult to state to what extent this is due to accelerator set-up resulting from difference in rate of cure and how much it is due to the inherent qualities of a carbon black. Consequently in the present paper, which is confined to fundamentals, we are limiting ourselves to the "Delta A function" as referred to a basic test formula.

The Test Formula

In the development of the data which are here presented the base mixing employed was: rubber, 100; litharge, 30; sulphur, 5; total, 135.

It might, at first sight, appear strange that a litharge test formula was selected, rather than one containing a typical organic accelerator of vulcanization. This was done, however, for the reason that each of the individual blacks was found to differ in its effect upon the commonly used organic rubber accelerators.

We believe that it is entirely impossible to draw any conclusion regarding the effect of pigments or other compounding ingredients upon rubber unless comparison is made under equivalent vulcanizing conditions. Trite as it may seem to introduce a remark such as the foregoing it is astonishing how often this point is not sufficiently stressed.

Selection of a state of vulcanization or optimum cure at which to compare samples presents problems by no means easy to solve and leads directly to the question, what are the proper cure criteria for work of this nature?

The object of pigment research applied to rubber compounding is to determine the effect of each pigment upon the various physical properties, and it is, therefore, obviously not in order to set up a fixed value for one of these, e.g., modulus, as the criterion for selecting comparable cures.

Regarding the matter of bringing all samples to a comparable state of vulcanization, there are three possible means of attack: (1) Compensation by changing the time of cure employed. (2) Compensation by changing the proportion of accelerator used. (3) Employment of a compound whose rate of cure is unaffected by the introduction of the ingredients under investigation.

The errors introduced may be enormous when attempts are made to compensate for varying accelerating or retarding effects through use of different periods of cure, principally because neglect of the set-up factor cannot fail to destroy all standards in such cases.

Changing the proportion of accelerator to compensate for the effect on cure of other ingredients is not unsound practice, but requires such nice adjustment of accelerator as to make this procedure a questionable expedient in pigment research.

The most valuable pigment studies thus far published have been those carried out with a flat-curing litharge mix as the base compound, and for this paper the litharge formula above indicated was selected in order to iron out the differing effects of the pigments under consideration.

In a preliminary way cure was established by hand-tear tests as employed by Dinsmore in his more recent papers, and for a control and check on these estimations combined sulphur determi-

nations were used. We have found by such means that the litharge compound employed does iron out the effect of the blacks on rate of vulcanization, and in a 40 parts by weight loading, for example, combined sulphur values for the five pigments under comparison, gave results as follows:

SAMPLE DESIGNATION	COMBINED SULPHUR
Sample No. 1.....	1.84
Sample No. 2.....	1.75
Sample No. 3.....	1.90
Sample No. 4.....	1.78
Sample No. 5.....	1.82

It is not the purpose of this paper to present an elaborate discussion of the methods available for determination of state of cure, and it seems necessary only to say in connection with the use of sulphur figures that although this determination has little, if any, value in estimating the cure of unknown samples or in differentiating between various states of vulcanization, it certainly does, however, serve as an indication that a series compounded from a given base is or is not uniformly vulcanized.

The significance of the stabilization effected by this type of mixing will be appreciated when it is understood that in formulas accelerated with D.P.G., and other organic materials, *it may be necessary to double the time of cure required to bring the fine reinforcing black to the cure condition of the filler type.*

The fact that carbons made by different processes have specific effects upon vulcanization is explained by differences in absorption activity. All blacks are produced under high temperature conditions since the basic reaction involved is thermal decomposition of hydrocarbon gas. Activity is conditioned on fineness of particle size, the degree of temperature and duration of exposure to temperature which the pigment undergoes following formation. Through regulation of manufacturing conditions the product of any given type of process may readily be held uniform but it naturally follows that blacks turned out by distinctly different methods differ in this respect. In practical compounding it is easy to adjust the amounts of organic accelerators to compensate for this, but different conditions must be met in the case of scientific study undertaken for the purpose of basic evaluation. Since litharge is unaffected by the absorptive capacity of the carbons it is the best accelerator for this fundamental work.

Dispersion

Next to the choice of a base compound, probably the most important factor affecting the tests is complete dispersion. This calls for different handling with each loading of the various sorts of black. Where there is 40 per cent or more of carbon to the rubber in a mixing very little additional precaution need be observed to assure similar dispersion of all the blacks. However, in the case of more complex formulas involving the use of reclaims, bitumens, emollients, etc., and also in a simple mixture containing a relatively small amount of black, more attention must be given to dispersion. Here, laboratory procedure follows the best factory practice, namely: use of master batches, or the nearest equivalent; addition of black to a sufficiently small pro-

portion of the total rubber and at a point before addition of softeners, so that the pigment is incorporated while the rubber is sufficiently firm to break down agglomerates which may form in packing, or by passage through the bite of the mill rolls.

The "Delta A Function"

For the present discussion the writers have chosen three commercial carbons and two experimental blacks, as follows: 1. Standard reinforcing carbon black. 2. Moderate reinforcing high yield carbon. 3. High yield soft carbon. 4. Experimental carbon black. 5. Experimental carbon black.

These blacks were mixed into the base compound in successively increasing proportions, cured as described and tested under uniform conditions of temperature and humidity.

In Figure 3 are shown the "Delta A function" for samples 1 to 3, representing blacks now in use in the industry.

We see that standard reinforcing carbon develops the highest energy at all loadings and that it has the longest range of useful loadings.

Carbon No. 2 exhibits moderate reinforcement over a fair range of loadings; while Carbon No. 3 is only slightly reinforcing.

It is interesting to note that the energy-volume loading curve for standard carbon in the fundamental base used, shows a distinct plateau effect from 40-50 per cent pigment loading on the rubber, which is in close agreement with tread compounding practice and experience with all types of organic accelerators, diluents, emollients, etc. Also, this is the only black suitable for use in very high loadings where extreme hardness and toughness must be combined, as in solings and special mechanical rubber goods.

The Class 2, or moderate reinforcing carbon, shows an optimum considerably lower and slightly earlier. Since this grade of black is comparatively new there is not the same background of experience to confirm its position as shown by the "Delta A function." However, so far as data are available they are in close accord with the present findings.

Sample No. 3, or the soft carbon, gives its best results as a diluent pigment, which is also confirmed by experience in many plants and compounds.

In Figure 4, are shown experimental blacks No. 4 and No. 5 against standard reinforcing carbon. No. 4 carbon exhibits a fair peak but its range of usefulness is somewhat short. No. 5, as it stands does not have much to recommend it to the rubber man since it develops neither high optimum energy nor long range of usefulness. However, it exhibits qualities distinctly different from the category employed as rubber fillers. Thus, it is seen that this method of evaluation is useful, not only in classifying successful commercial grades according to basic stress-strain qualities, but also that it is valuable in research and development work with new carbons, assisting as it does to differentiate between products which are commercially important and those which may have only a limited application, or which may be entirely unusable as they stand.

Quantitatively, the blacks here discussed are accurately summed up in Table 1, in which for convenience, the standard is designated as 100.

TABLE I

Black	Energy Capacity or "Delta A"
1 Standard reinforcing.....	100
2 Moderate reinforcing, high yield.....	64
3 Soft, high yield.....	35
4 Experimental	64
5 Experimental	21

Conclusion

In conclusion, it is shown that the "Delta A function" provides an instrument for the classification of carbon blacks as regards their usefulness to the rubber compounder. It is an index of widely inclusive character and not only indicates performance at optimum concentration, but also the range of effectiveness.

The writers have undertaken exposition of the special applications of this to the classification of carbon pigments, pointing out the precautions necessary for its accurate use. We believe it important to supplement the "Delta A function" with other stress-strain data, also with laboratory performance tests, and finally with service records, when it is necessary to differentiate between carbons of the same general category. On the other hand, we believe no study of carbons or other pigments is complete unless "Delta A" values are included.

Acknowledgment is gratefully made for the valuable suggestions of W. B. Wiegand and also the cooperation of Binney & Smith Co., who supplied all of the carbon blacks investigated and gave permission to publish the data covered by this paper.

Technical Application of Antioxidants

E. R. Bridgwater

IT is unfortunate that the process of vulcanization, to which the commercial use of rubber is almost wholly due, makes it much more susceptible to oxidation. The deterioration that sets in as soon as rubber is vulcanized was first attributed to oxidation by Miller in 1865 but it is only during the last 20 years that a serious effort has been made to find means of preventing it. During this period it has been found that many chemicals retard the oxidation of rubber when incorporated with it prior to vulcanization. Phenolic compounds, primary and secondary amines, amino-phenols and condensation products of aldehydes with amines are the chemical groups within which the most valuable antioxidants are found. Many amines and aldehydeamine condensation products are also vulcanization accelerators and some of the earliest known accelerators have a mild anti-oxidant effect. Para-phenylenediamine and para-aminodimethylaniline were used as accelerators long before the term antioxidant was coined and their favorable effect on the aging properties of rubber compounds has been a matter of common knowledge for more than ten years. Recent investigations have disclosed numerous compounds in these classes that have little or no accelerating effect and are far more effective in retarding oxidation than any of the known accelerators.

Within recent years, rubber chemists have come to realize that oxidation is by no means the only way in which rubber deteriorates nor is it always the most serious form of deterioration. The term "antioxidant" has been broadened to include all materials that prevent the deterioration of rubber, either in storage or in service, regardless of whether the deterioration is due to oxidation or to other causes. It has been suggested that it might be preferable to use a more inclusive term, such as "anti-deteriorant" to describe these compounds but the word "antioxidant" has become firmly established and there seems to be just as much reason for retaining it as there is for retaining the word "accelerator" to describe compounds that do much more than merely accelerate the vulcanization of rubber.

NOTE: Presented before the N. E. Section and Rubber Division, Boston Group, A. C. S., Boston, Mass., Jan. 12, 1929.

Reversion

One of the most serious forms of deterioration to which rubber is subject is reversion or devulcanization. It was formerly the custom to speak of the vulcanization of rubber as an irreversible reaction because the sulphur that combines with rubber during vulcanization can be removed only with difficulty, if at all. However, most rubber chemists now agree that the essential difference between vulcanized and unvulcanized rubber lies not in the degree of saturation but rather in the degree of aggregation. The combination of sulphur with rubber appears to be only incidental to the more significant physical changes that occur on vulcanization and those physical changes are certainly reversible. The tendency toward reversion is always present in vulcanized rubber but may not be apparent if the rubber contains an accelerator of the non-fugitive type and sufficient sulphur to permit vulcanization to continue at a slow rate, thereby counteracting the tendency toward reversion. Accelerators that are destroyed during vulcanization are usually referred to as fugitive, while accelerators that are not destroyed and cause vulcanization to continue as long as free sulphur is present, are termed "non-fugitive."

Blooming compounds have less tendency toward reversion than non-blooming compounds, other factors being equal, because the free sulphur causes vulcanization to continue at a sufficient rate to at least partially counteract the tendency toward reversion. It is therefore apparent that after-vulcanization is not necessarily harmful and an ideal rubber compound is one that continues to vulcanize at a rate just sufficient to counterbalance reversion. On the other hand, one must guard against the use of non-fugitive accelerators in high sulphur compounds because the rate of after-vulcanization may be so great as to more than counteract reversion and therefore cause the rubber to become stiffer, harder and shorter as aging proceeds.

Anti-Softeners

Some antioxidants have a stiffening effect on rubber even in the absence of free sulphur. Benzidine and meta-tolylendiamine are outstanding examples of this class of compounds to which the term "anti-softener" has been applied. Their effect is quite pronounced even when used in exceedingly small quantities and, because their efficacy does not depend upon the presence of free sulphur, they are of great value in preventing the reversion of low sulphur non-blooming compounds.

Reversion may, of course, be caused by overcuring low-sulphur compounds. The reversion that occurs on overcuring differs only in degree from that which occurs during aging. The time-honored way of preventing reversion on overcure is to use sufficient sulphur so that it will not be entirely ex-

hausted before the cure is completed. This is, however, a satisfactory solution of the difficulty only when a non-fugitive accelerator is used. The tendency toward reversion on over-cure may be greatly reduced by using an anti-softener, in order that the rubber may tend to continue stiffening even after the sulphur is exhausted, thus counteracting the tendency toward softening or reversion.

Tension-Cracking

There is another type of deterioration that is less well understood than oxidation and reversion but is often of even greater importance. Common examples of it are the cracking of boot uppers at the point where they are folded when placed in the shipping carton; the cracking of pneumatic tire treads at the base of the design or ribs; and the cracking of rubber soles due to the tension on the rubber around the stitches and across the ball of the foot when the sole is flexed, as in walking. This type of failure occurs wherever rubber is held under tension for a long period, as in the case of boot uppers that are folded, or when rubber is alternately stretched and released, as in the case of pneumatic tire treads. It will be noted that cracking always occurs in tire treads at the point where the stretch is greatest due to the distortion of the tread design that is caused by the weight of the car and by the transmission of power through the rear tires. Highly compounded stocks ordinarily crack more readily than less heavily loaded compounds.

This form of deterioration appears to be quite unrelated to oxidation. It is, of course, true that rubber oxidizes more readily when it is stretched but it is clear that oxidation is not the only cause of "tension-cracking" because many materials that are good antioxidants are of little value in preventing tension-cracking. The friction and skim coat stocks which bind together the plies of a pneumatic tire or a power transmission belt are also subjected to tension in service because of the tendency of the plies to move relative to one another when a tire is flexed or when a belt passes over its pulley. It is therefore not surprising that the same materials which retard the cracking of pneumatic tire treads or boot uppers are also effective in decreasing the tendency toward ply separation in pneumatic tires and in transmission belts.

It may or may not be a mere coincidence that the most effective compounds that are known for retarding these forms of deterioration are also powerful oxidation inhibitors. In any event, the term "antioxidant" is being used, even when the primary purpose for which the chemical is added is not to inhibit oxidation but to prevent the cracking of treads or to retard the tendency toward separation of friction and skim stocks. Among the most effective compounds for this purpose are phenyl-alpha-naphthylamine and phenyl-beta-naphthylamine. In some cases it has been found desirable

to use a small percentage of an anti-softener such as meta-tolylenediamine in conjunction with phenyl-alpha or beta-naphthylamine. A few examples of the uses to which this class of compounds has been put will probably be of interest. It has been found that the life of airbrake diaphragms may be more than doubled using phenyl-alpha-naphthylamine combined with meta-tolylenediamine in the friction and skim-coat compound. The life of the diaphragm in this case is measured by alternately applying and releasing air pressure, as in service, until separation occurs. In another case, it was found that the time that a fan belt would run before the plies separate could be increased by approximately 60 per cent due to the addition of phenyl-alpha-naphthylamine and meta-tolylenediamine. In highly compounded black soles it appears that the tendency toward cracking can be greatly reduced by the use of these chemicals. Their major use is, of course, in pneumatic tires—in the tread for the prevention of cracking and in the carcass stocks because they decrease the tendency toward ply separation.

Sun-Checking

Tension-cracking must not be confused with sun-checking. Reference has been made above only to the type of cracking that is caused by mechanical stresses alone. Sunlight and ozone cause rubber to crack or check, which cracking is accelerated by stretching the rubber but, so far as the writer is aware, no compounding ingredient is known which will prevent this type of failure with the exception of materials that bloom to the surface, forming a protective coating. Paraffin wax is the most widely used and probably the best material for mitigating the harmful effect of sunlight, although it falls far short of being a perfect remedy.

Testing Methods

The above examples are sufficient to illustrate the significance of the new and greatly broadened meaning of the term antioxidant and it is suggested that the manifold functions of antioxidants should be borne in mind by all those who are engaged in the testing of rubber. If the only purpose of an antioxidant were to prevent the combination of oxygen with rubber, it would seem that the proper way to test antioxidants would be to determine the rate of increase in weight when samples are exposed to air or, still better, to oxygen in the Bierer-Davis bomb. Many workers in this field have based their conclusions with respect to the efficacy of antioxidants solely upon the rate of change of tensile strength, elongation and stiffness of rubber samples during aging in the air at elevated temperatures or in the oxygen bomb. This practice is open to serious criticism because such tests give no information with respect to the efficacy of a product in pre-

venting the cracking of tire treads or shoe soles or decreasing the tendency toward separation in carcass stocks.

It seems obvious that the properties which should be measured are those which actually come into play in service and that they should be measured both before and after aging in air or in the oxygen bomb. Tensile strength is a factor of little importance in the case of coated fabrics. It seems, therefore, that the best way to test them is to age them in the oxygen bomb and compare the flexibility and elasticity of the rubber coating before and after aging. It is suggested that antioxidants for shoe soles be tested by sewing the soles on to a leather belt which is run at high speed around small pulleys, the test being conducted on both aged and unaged samples in order to determine not only the effect of the antioxidant on the aging properties of the compound but its effect on the tendency toward cracking of fresh soles as well.

It seems not unlikely that the discovery of materials which retard separation in pneumatic tire carcasses, belts, etc. will make it possible to use larger percentages of reclaimed rubber than has heretofore been practicable in such compounds. Certainly, it is no longer necessary for tire manufacturers to limit the hardness of tread compounds for the purpose of preventing cracking and it may now be found that more heavily loaded tread compounds could be used to advantage. On the other hand, there are other factors than tread cracking which make it inadvisable to use a too stiff compound for a tire tread.

Sufficient work has not yet been done to show why the materials that we call antioxidants prevent the cracking of rubber and retard separation, but the discovery that they do opens up many new possibilities in mechanical goods and specialties as well as in tires, and certainly offers a most fertile field for further research.

Measuring Temperatures of Calender Rolls

L. R. Keltner

IT has only been within recent years that the importance of knowing the exact conditions under which rubber is processed has been appreciated. This is especially true of the calendering operation. For many years a calender man's experience was the only assurance one had of producing properly processed material. Demand for greater uniformity of product now necessitates more uniformly processed materials. The ultimate outcome of these demands was the setting up of a definite set of mixing and calendering specifications.

It is readily recognized that a calendering specification would not be complete without some reference to the calender roll temperature. The effect of heat on rubber processing cannot be discussed here but it should be stated that it is of tremendous importance. The need for a roll temperature measuring device thus presented itself and various types of instruments have been experimented with.

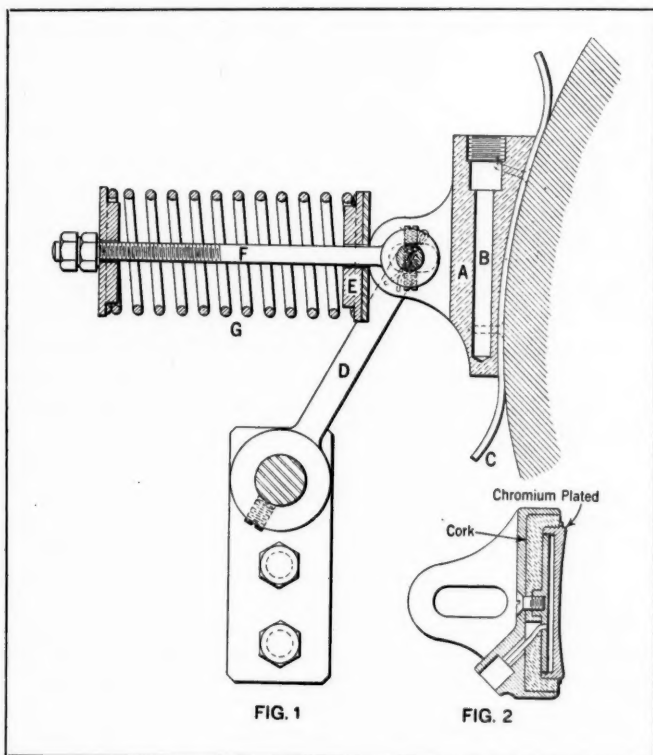
Early experiments were made in a crude manner by attaching the hot junction of a thermo-couple to a small 1-inch square brass plate which was mounted on a yard stick. This stick was used as a lever and a cross bar from the calender housing as a fulcrum. After the brass plate had been placed at the desired spot on the roll, pressure was applied by pulling up on the end of the stick opposite the junction. Data obtained were satisfactory but the apparatus had no practical application in production. Other experiments along the same line were carried out later.

In one of these arrangements the hot junction was attached to a shoe whose duraluminum face was concave to fit on the surface of the roll. The leads from the couples were attached to a pyrometer whose indicator was calibrated on a temperature scale and a reading was automatically recorded on a chart every minute. The system was electrically actuated throughout. This apparatus was fairly satisfactory in the laboratory although some trouble was encountered in holding a calibration and in keeping rubber from dislocating the shoe.

NOTE—Publication permitted by *Ind. & Eng. Chem.* Paper read at the Akron Group Rubber Division A. C. S. meeting held in Akron, O., Dec. 3, 1928.

During this experimenting several factors presented themselves as necessary features of any instrument which was to be used in production. They are as follows: (1) It must be rugged and durable. (2) It must not be dislocated by rubber. (3) It must be fairly accurate. (4) It must be easily maintained.

These features seem best contained in the apparatus which we are using at the present time, as shown in Figure 1. It consists of a manganese bronze shoe *A* drilled to fit an expansion system thermometer bulb *B*, and faced with a zinc



wearing strip *C*. The strip is concave, fitting the calender roll and has a reverse radius at both ends. These rounded ends prevent any stray rubber from catching on the shoe. The shoe is held in position by the arm *D*, which is bolted to the calender housing. On the back side of the shoe is welded a spring seat *E*, through the center of which protrudes a tension rod *F*. At the threaded end of this rod, two hex nuts and a washer may be adjusted to supply the tension on the spring *G*. The other end of the tension rod is joined at the shoe to the curved end supporting arm *D*. This allows the shoe

about $\frac{1}{4}$ -inch movement against the spring and thus releases it from the calender roll when any irregularity on the roll surface occurs. The bulb of this apparatus is attached through an armored tube system to a temperature recorder of the proper range.

The apparatus is rugged, seldom requires attention and is not easily dislocated. Heat losses due to radiation and conduction are partially compensated by heat generation due to friction of shoe to roll. Variation in temperature is approximately 5° .

An improvement in this apparatus has recently been designed by one of the instrument companies and is shown in Figure 2. The changes in design of the apparatus as compared with Figure 1 are in the expansion system. In this diagram, we show a cavity built directly in the shoe. It is closer to the surface of the roll and is insulated by approximately $\frac{1}{4}$ -inch of cork. This should give even better results.

Another instrument used in experimental work is the Cambridge hand pyrometer. This portable pyrometer consisting of a bi-metallic band so attached to galvanometer connections that it will assume the curvature of the roll when pressed against its surface has also proved of value in taking roll temperatures. The instrument in its present form is not properly compensated for variations in room temperatures and will give accurate readings, only if they are corrected according to the proper calibration curve for the specific room temperature at the time used.

Goodyear Experience in Temperature Control of Mill Rolls

R. W. Moorhouse

GOODYEAR TIRE & RUBBER CO., AKRON, O.

IT is well known that in milling a batch of rubber or compounded stock, the temperature of the mill rolls rises—rapidly at first, then more slowly—to a given temperature at the end of the run. There are, however, a number of factors which affect in varying degree not only the temperature eventually reached, but the intermediate temperature of the roll surfaces. Of these we may form two groups, those tending to increase and those tending to decrease the temperature.

Factors Affecting Roll Temperature

Initially high temperature of batch, toughness of the rubber or stock, heavy loading, large bank and gage and increasing ratios of roll speeds, tend to increase the temperature. Merely starting the average cold rubber through the mill increases the roll temperature 15° F. in the first five minutes, while using hot stocks increases this to 20° F. in two minutes.

Toughness of stock affects roll temperature by varying the amount of heat produced in the first few minutes of milling, the rise of temperature increasing with the tougher stock.

Doubling the gage of the mill increases the roll temperature 10° F., due to increased working of the batch. The same effect is obtained by increasing the size of the batch, up to the point of producing an idle bank.

As small a change of ratio as from 1.11 to 1.17 will produce a rise of 10-12° F. in roll temperature.

Cooling may be obtained, but only momentarily, by the addition of cold compound or a little water to the stock on the mill.

Of far more importance in lowering the roll temperature is the more efficient use of more and colder water. We are limited in the Akron district in amount of water, as well as

NOTE—Publication permitted by *Ind. & Eng. Chem.* Paper read at the Akron Group Rubber Division A. C. S. meeting held in Akron, O., Dec. 3, 1928.

by seasonal temperature variation, unless we resort to circulation of refrigerated water. This is not considered the correct solution with present conditions at Goodyear, although certain other plants have found it practicable.

A further handicap in temperature control is the very great time lag between roll surface and cooling water temperature changes. In the average thick-walled roll, this varies from five to ten minutes; in the new thin-walled rolls from one to two minutes.

Temperature Measurement

Formerly the roll temperature was gaged by the hand, and by the appearance of the batch. More recently we have used thermocouples in one form or another, such as the Cambridge, the Thwing and the Bristol portable pyrometers. While in isolated cases we have used a fixed type of instrument, the portable type is preferred, since conditions at a

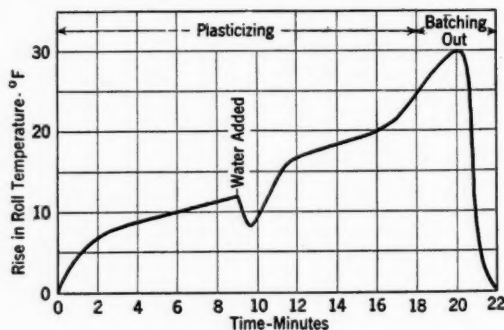


Fig. 1.—Plasticizing

mill give rise to considerable risk of damage to fixed equipment.

The use of any surface temperature indicator is complicated by the fact that the roll surface is moving at a relatively high speed and carries with it an invisible film of rubber or stock particles. These factors tend to neutralize each other, as the speed generates frictional heat in any instrument contact, while the film partially insulates the contact from the roll. The net effect on temperature has been found to cause as much as 14° F. difference between moving and stationary rolls. Besides this, the motion of the roll increases the cooling rate where exposed to the air, and carries a film of air between the contact and the roll, still further lowering the indicated temperature.

There is also a variation in temperature across the face of the roll, due to varying thickness of metal, conduction of heat into or from the journals and uneven distribution of cooling water. Dirt and slime in rolls and spray pipes are

responsible for poor distribution of water, causing variations as great as 25° F. In the case of a constant stock-feed mill, that point of the front roll from which the feed strip is being

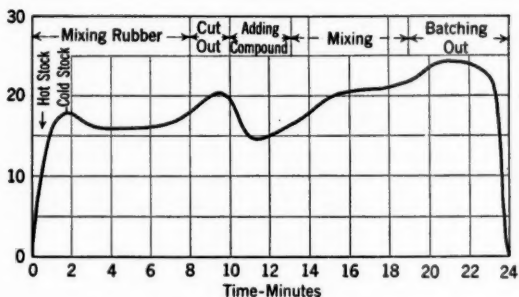


Fig. 2.—Hot Mixing

taken runs from 10 to 15 degrees hotter than the rest of the roll, probably due to increased working at this point.

Differences between front and back rolls have been found as high as 20° F., with equal water flow. This will vary from mill to mill, but is reasonably constant for the same mill with the same stock.

The errors and variations mentioned are far larger than those obtaining in measuring temperatures of fixed surfaces, which average 5-7° F. for thermocouples.¹ The errors of measurement, incidentally, are traceable entirely to the contact as any of the instruments used are correct within 1° F.

Temperature Cycle

Different milling operations, due to different combinations of the factors noted above, show definite roll temperature

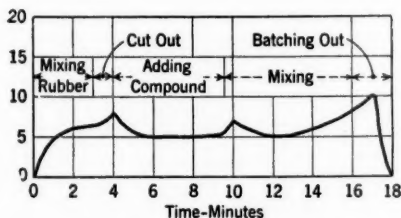


Fig. 3.—Cold Mixing Tread Stock

"cycles," characteristic of the particular operation. Temperatures of the middle of the back roll were taken with the Bristol portable pyrometer, and are plotted against time in the accompanying curves.

¹ Bauer & Buss, *Ind. Eng. Chem.*, 18, 728. Adams & Kean, *Ind. Eng. Chem.*, 18, 856.

Figures 1 to 5, inclusive, illustrate typical cases of plasticizing, hot and cold mixing high black stocks, cold mixing a high zinc stock, and mixing a coat stock with a large amount of well-plasticized rubber.

The steady increase of roll temperature in plasticizing is very evident, the addition of water only momentarily checking it. Even more rapid is the increase when slabbing off is started.

We can see plainly in the mixing curves the heating effect of the first addition to the mill and of working down the bank by cutting out and by batching off. The cooling effect of adding the compound, followed by the heating up as the compound works in and as the cut-out is replaced being quite visible. The quick drop after the batch has been taken off is very noticeable.

The temperature ranges vary from about 5° F. in mixing soft coat stock to 30° F. in plasticizing rubber. The rate of change of temperature varies from 2 to 10° F. a minute,

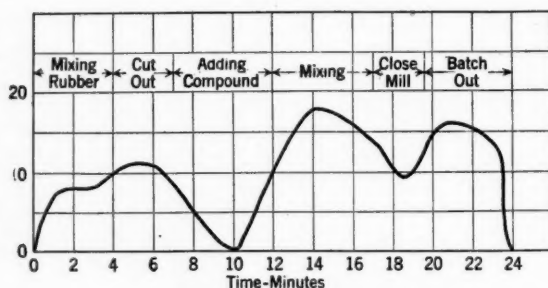


Fig. 4.—Heavily Loaded Stock

the greatest rate being found at the start of hot mixing, and in the final cooling period after slabbing off.

Figure 6 shows the heating of a constant feed mill operating on a tread stock. There is evident a considerable range —40° F.—of surface temperature and a rapid cooling after each run, both of which conditions make for considerable variation in stock.

Advantages of Control

While these curves show the actual ranges obtaining in practice with the standard uncontrolled mill, they cannot be considered as ideal for the operation in question. Too cool a mill, even in the case of a feed mill, will lower plasticity, while too hot a mill permits too much of the original toughness to remain in the finished stock. There exists, therefore, an uncontrolled variation in stock quality aside from that already present.

A total range of mill roll temperature of 15°F. is considered the maximum for production of uniform stock. The location of this range will, of course, vary with the stock, from a start of 110°F. or lower for breaking down, to a start of 130°F. for mixing and warming up tube stocks. Feed mills are best operated on even closer specifications, a

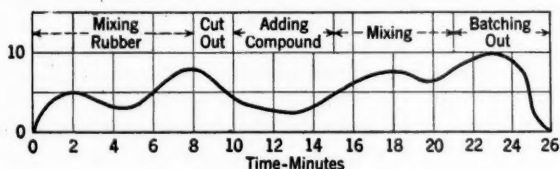


Fig. 5.—Mixing Coat Stock

difference of 5°F. between calender and mill being the desirable maximum.

Aside from the advantage of stock uniformity, there is increased efficiency in the use of water, a point of no small value to us in the Akron district. There is also a saving in actual water used, since no water is used between batches.

Methods of Control

There is but one way to control the variation of temperature in a mill, *i.e.*, to vary the cooling capacity of the water fed into the rolls. There are, however, several ways to vary the cooling capacity, which depends upon the amount and

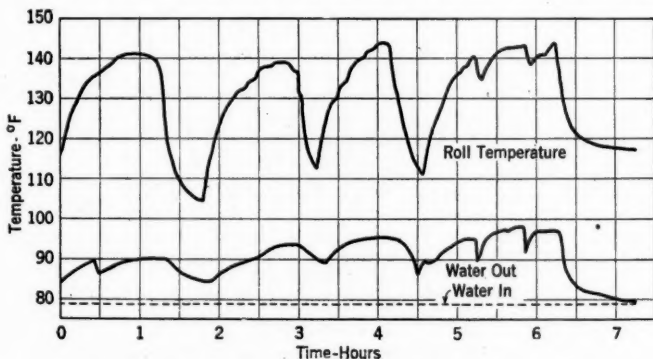


Fig. 6.—Feed Mill Temperature Constant Water Flow

temperature of the water and the manner of its application.

The simplest and least satisfactory control is by reading the temperature with a portable pyrometer and manually changing the setting of the water valve. The labor involved is enough to make this method uneconomical for close control, as the change in temperature is seen to be very rapid in

every type of operation. This method can be used, therefore, only to fix approximately the location of the temperature range at which the mill operates. At Goodyear, we have made measurements several times a shift, adjusting the water valves to give more or less water, according to the readings and the stock being worked. The net result is a balancing of the water supply according to the characteristics of the mills, with a general increase in mill room efficiency.

Continuous control means, therefore, automatic equipment, such that as the rate of heat delivery to the roll changes, the rate of heat removal changes proportionally. Since the roll temperature controls and indicates the rate of heat delivery, an automatic water control operating from the roll surface should give good temperature regulation.

Equipment was, therefore, constructed, using a standard Tycos controller, the bulb carried in a bronze shoe riding on the back roll of a feed mill, and the controller operating a reverse-acting diaphragm valve on the water feed line. The mill was used for obtaining the data for Figure 6, and was operated under similar conditions. Several runs were made and the results plotted in Figure 7. The temperature with the stock on the mill was 120°F. , after the roll had warmed up. However, while the water was shut off several minutes

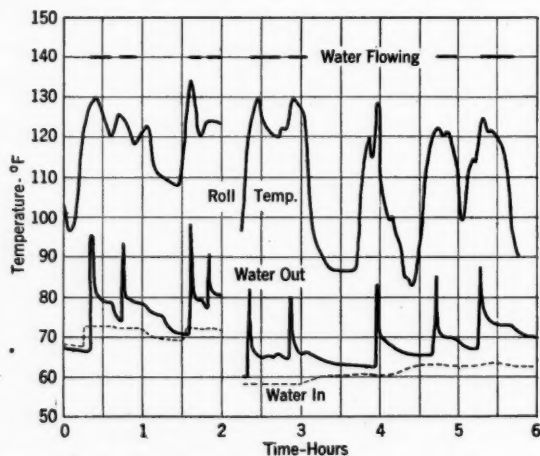


Fig. 7.—Feed Mill Temperature with Control from Roll Surface

before the stock was run off, the roll continued to cool, due apparently to the large amount of cold water still in the roll. This caused a period in the next run during which the stock was milled on a cool roll, a condition no better than that obtaining in the uncontrolled roll of Figure 6. It is possible that reducing the head pressure on the water

line (and hence the water flow) will cause less variation in the water temperature within the roll, and therefore less roll temperature variation between runs. A direct-acting diaphragm valve will also tend to eliminate sudden and wide fluctuations within the roll. As it was, the controller gave

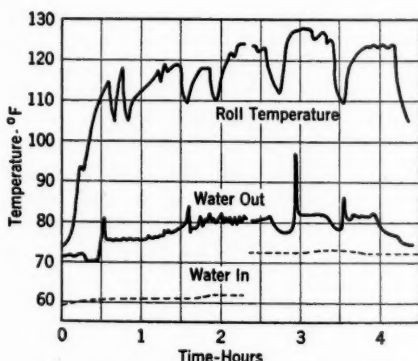


Fig. 8.—Feed Mill Temperature with Controlled Water Temperature

a rise in roll temperature three times as fast as the uncontrolled roll together with a lower maximum temperature and a much lower water consumption.

Since roll surface operation of the controller caused large fluctuations in the outlet water temperature, as shown by the lower curve in Figure 7, control of this temperature was tested. Two air-operated controllers, made by the Bristol company,² were attached to the same mill, and runs made under the same conditions as before. While it was believed that the lag from surface to water would increase the variation in the surface temperature during a run, we found that this variation was reduced to about 5° F. The cooling between runs, instead of being 40° F. as in the two previous tests, was only 20° at its maximum. Further, the roll heated up equally as fast as with the surface control. Water consumption was approximately that of the surface control, and the outlet temperature was far more uniform, indicating increased efficiency.

Future Development

While the methods of automatic control detailed above have yielded very encouraging results, especially in water saving, there is room for improvement in the elimination of the cooling between runs.

² INDIA RUBBER WORLD, July 1, 1927, p. 201.

Since the temperature of the stock on the mill is, in the ultimate analysis, the important item, its continuous measurement and means to use this measurement to automatically control the flow of cooling water become of prime interest. This problem requires some further study of equipment. It may depend for its solution on the use of radically different methods of cooling mills having much thinner walls than any now available. The successful solution of the problem, however, will repay the effort, in the elimination of one of the troublesome factors in the industry, the interference by hot mills with continuous production of sensitive stocks.

Thanks are due to the Goodyear Tire & Rubber Co. for the opportunity to present this paper, and to C. H. Smith of our organization for his work in collecting a large part of the data.

Contribution to the Thermochemistry of Rubber

Siegfried Boström

DISSERTATION, UNIVERSITY OF GIESSEN, 1927

Introduction

The object of the present work is the application of thermochemical methods to the scientific and technical problems of rubber. As this is a new field, it was encouraging to recall that few difficulties presented themselves. Variations in the results of about ten per cent were permissible due to the indefinite character of the material, the slow course of the reactions measured, faulty apparatus, and imperfect technique. Further work will be done in the physical chemical laboratory at Giessen to render the methods more precise, to discover sources of error, and to avoid those not inherent in the nature of the work.

The thermostat for the differential calorimeter used in the experiments (see Figure 1) consisted of a double-walled cylindrical vessel, Th, of zinc plate, 60 cm. high and 35 cm. diameter. For higher temperatures the liquid between the walls of the thermostat could be brought to a boil. At room temperature the thermostat could be used without the heating jacket, as the layers of asbestos and paper surrounding it and the stagnant air between the walls offered sufficient protection from the influence of the temperature without. A cover, D, could be lowered into the thermostat from above. This was also made of zinc plate, 20 cm. high and 24 cm. wide. By means of an immersion heater, liquid could also be brought to a boil in this cover. Through it passed two tubes, R, which could be closed at both ends and which served to introduce the reaction vessel into the calorimeter. Through an opening in the middle, O, the double agitator, *r*, could be operated.

The differential calorimeter consisted of two polished copper Weinhold beakers, W₁, W₂, and a thermopile of 36 thermocouples. The thermopile was mounted on a marble plate, M, which had semicircular pieces cut out at each end, the diameter of which was 2 cm. smaller than the diameter of the beakers. Thin glass tubes passing through holes at the edge of the concave portion of the slab contained the elements of the thermopile and were held in place with a litharge-glycerine mixture. The tubes and, therefore, the elements were arranged in two rows in such a way that at one end of the semicircle one row began with a long tube that reached just to the bottom of the beaker, alternating and finally ending with a short tube that reached only a centimeter below the surface of the liquid. At the other end of the semicircle the second row also began with a long tube and ended with a short one. By using this form of thermopile, there was relatively more room available in the middle of the vessel for the substance under examination. Moreover, in this way the thermocouples were distributed among all the layers of the calorimeter liquid, a feature which is quite essential for the measurement of the heat effects that occur. The thermopile may be placed rider-like over both beakers. The elements of the thermocouples were strong, 0.5-mm. iron and constantan wire, joined together with silver solder. To protect the wires against moisture and vapor, they were dipped in a rubber solution, were then treated with very dilute sulfur chloride, and finally were washed with soda. To insulate the constantan wire from the neighboring iron wires, it was placed in a very fine glass tube. Glass

beads would have been better. To permit better heat transfer from the calorimeter liquid to the thermocouples, some mercury was poured into the tops of the glass tubes and around the couples. Finally the mercury was covered with a layer

of paraffin. The lead and return wires on the marble slab were insulated by mica plates. The ends of the thermopile led to clamps attached to the slab. On both sides near the middle of the concave portion there was a glass tube 0.6 mm. thick, sharply bent in a U-shape, through which passed a manganese spiral wire 120 cm. long, whose resistance at room temperature was 6991 ohms in one case and 7650 ohms in the other. To facilitate heat conductivity, these tubes were filled with paraffin oil. The ends of the heating coils were soldered to copper wires leading to clamps on the marble slab. The double agitator, which stirred both beakers simultaneously, was made in such a way that as much room as possible was left for the reaction vessels. It was made of brass, except the connecting piece between the two stirrers, which was of slate to diminish the heat exchange between the two vessels. A glass stirrer served for the experiments with sulfur chloride.

The temperature difference in the two beakers was measured with a Siemens & Halske galvanometer, the sensitivity of which was about 10^{-9} amp. One mm. on the scale corresponded to about 0.001°C . In order to avoid secondary thermal effects, the leads from the thermopile to the galvanometer were covered with rubber tubing and a Peschel tube. The galvanometer for similar reasons was inclosed in a lead case with an opening to permit readings.

The apparatus was standardized after each experiment by heating electrically. The current for the heating coils was taken from a storage battery of large capacity and

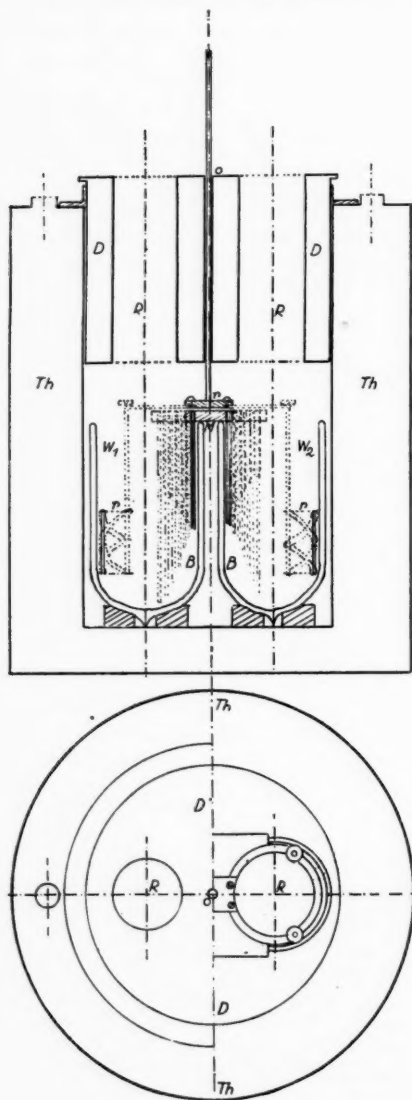


Figure 1—Thermostat¹

constant voltage, and was regulated as closely as possible by means of a variable resistance so that the duration of heating and the temperature difference produced in the vessels were the same as in any preceding reaction. During heating

the amperage was measured by a Universal galvanometer which permitted reading to 10^{-3} amp. and which was compared with a standardized instrument. Unfortunately no compensation apparatus or precision voltmeter was available, otherwise the energy expended in heating could have been calculated as the product of the voltage times the amperage. As it was, the calculations involved the square of the error in measuring the amperage. The time of heating was measured with a stop watch. The wires for the heating current were passed through a hole in the thermostat to clamps on the marble slab, care being taken to avoid current losses and induction effects.

Method for Determining the Activity of Rubber Fillers

In the rubber industry not only do fillers serve to dilute or color the raw rubber, but there are a number of "active" fillers which have a great influence on the physical properties of the mix. Wiegand² studied the relations involved by system-

TABLE I

Sample number	Type of black	Heat of wetting Q in cal. per gram black	Average of Q	Relative surface Micronex 100
1	Dixie black	3.85 4.04 4.20 4.20	4.07	145
2	Air-floated black	3.77 4.09 3.69	3.85	137
3	Micronex	2.85 2.68 2.86	2.80	100
4	Lampblack No. 1	1.25	1.25	44.6
5	Lampblack No. 2	1.15 1.21	1.18	42.2
6	Lampblack No. 3	1.06 0.96	1.01	About 36.0
7	Lampblack No. 4	1.05 0.92	0.98	
8	Lampblack No. 5	1.09 0.85	0.97	
9	Lampblack No. 6	1.01 0.91	0.96	
10	Lampblack No. 7	0.51 0.53	0.52	18.5
11	Thermatomic carbon	0.08 0.04	0.06	2

atically preparing compounds of rubber and various fillers and determining the resilient energy (work required for rupture).³ He was able to show by these experiments that the surface of the filler is of extreme importance.⁴ The effectiveness of a filler increases with increase in the total particle surface and therefore with increase in particle fineness.⁵ Hitherto particle size has been determined directly by measuring under the microscope or by mixing the particles with water and allowing them to settle.⁶ Pouillet's observation⁷ that the wetting of a dry powder develops heat has, however, afforded us another way of evaluating fillers, as the heat tone is a surface phenomenon. This method has the advantage of giving the average of a large number of particles, whereas the measurement of a few particles under the microscope seems more or less haphazard. Berl and An-

deresz⁸ have already used this method in the examination of activated carbon by wetting 1.5 g. of carbon with 10 cc. benzene. They were interested in determining the "inner surface," whereas in the following experiments an inner surface need not be considered because of the small particle size and, therefore, the relatively large outer surface. Thus far no serious objections to this assumption have appeared. The first preliminary experiments were with a series of carbon blacks.

The experimental details were as follows. The reaction chamber consisted of a brass cylinder 10 cm. high and 2.5 cm. wide. On the bottom there projected a small brass tube 2 cm. long and 1 mm. internal diameter. An iron wire covered with water glass was stuck into this little tube so that the cylinder was completely closed below. Above, the reaction vessel was closed by a cork stopper in which there was a glass tube 0.5 cm. thick, which served as a handle for the reaction vessel, and also permitted the removal of the iron wire from the thermostat. About twenty grams of black, previously dried at 100° C. and kept in a desiccator, were placed in the brass cylinder. To facilitate heat transfer, a brass plate was placed in the midst of the carbon black. The reaction vessel was then placed in the calorimeter, which was filled with benzene, and when the temperature reached equilibrium the iron wire was drawn out so as to permit the benzene to come in contact with the black. Table I gives the heats of wetting per gram of the various blacks.⁹ [A representative experiment, which is described in the original with calculations and quantitative data, is omitted.—Translator.]

The values obtained vary directly as the surface area of one gram of the black, and indirectly as the particle radius. For if one thinks of a black as a sphere with a mass of one gram and a specific volume $v = \frac{4\pi r^3}{3}$, then the radius of this sphere is $r = \sqrt[3]{\frac{3v}{4\pi}}$. If one divides such a sphere into m or n little spheres, then in the

first case the radius is $r_m = \frac{1}{\sqrt[3]{m}} \cdot \sqrt[3]{\frac{3v}{4\pi}}$, and in the second case $r_n = \frac{1}{\sqrt[3]{n}} \cdot \sqrt[3]{\frac{3v}{4\pi}}$.

The total surface of all the spheres in the first case is

$$O_m = 4m \cdot r_m^2 \cdot \pi$$

and in the second case

$$O_n = 4n \cdot r_n^2 \cdot \pi$$

The ratio of the radii is therefore $\frac{r_m}{r_n} = \sqrt[3]{\frac{n}{m}}$

The reciprocal being the ratio of the surfaces

$$\frac{O_m}{O_n} = \frac{m}{n} \sqrt[3]{\left(\frac{n}{m}\right)^2} = \sqrt[3]{\frac{m}{n}}$$

If one compares these results with technical experiences with the various blacks, agreement is unmistakable, as the various blacks must be arranged in the order given in Table I with respect to their capacity to increase the ability of a base mix to take up energy (reinforcement). However, it must be observed that, though the sequence is the same, in technical evaluation the differences would be less than indicated by the figures in the table. For it is found that the reinforcing effect of a black is not proportional to the degree of fineness. This may be explained by the fact that in preparing mixes on the mill the incorporation of the carbon black in the rubber is not complete enough so that each particle of black is completely surrounded by rubber, but rather the particles of black are distributed in the rubber to form comparatively large flocks. Apparently the larger

the particles the more perfect is the degree of dispersion. With increasing particle fineness the relative surface wetted by the rubber must decrease. As the activity of a filler is a function of the surface, a large part of the surface of the black does not come in contact with the rubber at all, so that the heat of wetting of the various types by benzene can be but a very rough measure of the activity in a mix. The carbon black can have a reinforcing effect through the operation of interfacial forces only to the extent that it is wetted by the rubber and adheres to it.¹⁰ A portion of the work of mixing apparently is used to bring about such adhesion. These forces of adhesion which become effective when the black is wet by the rubber can be considered the source of the activity.¹¹

To measure this surface energy, films of crepe milled for ten minutes were cut in small pieces and subjected to the action of benzene under the same conditions as with carbon black. To facilitate heat transfer, steel shavings were distributed among the rubber particles. It was found that when benzene is allowed to act on rubber in this way, heat is absorbed. This was strange as in the literature there are only examples which indicate that swelling—this is at least the predominant process here—is always accompanied by the evolution of heat.¹² We shall not discuss here whether we are dealing in this case with a swelling process only or to what extent several effects are superimposed. However, it is of great importance in these experiments that the action of benzene upon rubber in about three-quarters of an hour reaches a point where no further heat effects occur. The rubber has a swollen appearance, the individual slimy pieces may be compressed between the fingers; yet during this time nothing has gone into solution, for the benzene used may be distilled without residue. On swelling, one gram of the milled crepe consumed an average of 1.64 calories.¹³

Next, mixtures were prepared with 72% rubber and 28% carbon black, and subjected to the same treatment as the pure crepe described above. The heat effect observed on swelling these mixtures was apparently composed of:

- (1) The heat of swelling of rubber in benzene;
- (2) The heat of wetting of the carbon black by the benzene;
- (3) The energy used to overcome the adhesive force between the rubber and the carbon black.

It is the last feature which is concerned here. To determine experimentally whether these theories actually corresponded with the facts, mixtures were prepared using Miconex, No. 4 lampblack, and Thermatomic carbon. The results are given in Table II (1-3), and the data calculated therefrom (4-6). As the heat of swelling observed in 1 is not composed of the sum of the heat of swelling of the rubber contained therein and the heat of wetting of the black therein, the difference $[1-(2+3)]$ is obviously the "heat of separation" required to loosen the rubber / black bond.

According to 6, the various types of black are closer together with respect to their activity in a mix than in Table I, and this better accords with actual experience. Not only is this agreement qualitative, but, as far as may be judged from the material at hand, there is a quantitative agreement with Wiegand's results. The latter may be described briefly. Wiegand plotted stress-strain curves of vulcanized compounds containing 20% of various fillers, the ordinates representing the tensile, the abscissae, the elongation. The area between the curve and the abscissa, representing the work required for rupture, he called the "resilient energy." The values obtained by planimetric measurement of the area under the curve were then compared with the resilient energy of a base mix which did not contain the filler in question. Wiegand was able to show that the addition of fillers to the base

mix could increase or decrease the work required for rupture according to which fillers were used and what quantity thereof. Carbon black increases the tensile and the ability of a mix to store up energy. If the increase in resilient energy, expressed by Wiegand in foot-pounds per cubic inch, is calculated in calories per gram, there is obtained for Micronex the value 3.4 calories per gram.¹⁵ Unfortunately Wiegand's table does not show the other values for the carbon blacks examined. However, if we may be permitted to conclude, on the basis of the marked similarity between Thermatomic carbon and zinc oxide, that equal volumes cause the same increase in resilient energy, then we may ascribe to Thermatomic carbon an increasing effect on the work of rupture of 1.44 calories per gram as cited for zinc oxide (Luff).

TABLE II

	Micronex	No. 4 lampblack	Thermatomic carbon
1. Observed heat of swelling of rubber/black mix, per gram mix	1.30 1.27	1.37 1.30	1.63 1.50
	1.28	1.34	1.53
2. Observed heat of wetting of black by benzene (calculated on the quantity of black con- tained in 1 g. mix)	-0.84	-0.26	-0.02
3. Observed heat of swelling of rubber by benzene (calculated on the quantity of rubber con- tained in 1 g. mix)	1.18	1.18	1.18
4. Heat of wetting of rubber/black mixture per gram black (calculated from 1, 2, and 3)	-3.35 ¹⁴	-1.50	-1.32
5. Ratio of the surface of the black wettable by benzene (calculated from Table I, Micronex 100)	100	31	2.7
6. Ratio of the "activity" of the black in admix- ture according to 4 of this table, Micronex = 100	100	45	39

It should be noticed that Wiegand's figures differ more if based on one gram of rubber instead of on one gram of mix. Therefore, the resilient energy values would exceed the heats of wetting given in Table II. Still this fact need not detract from the belief that both values characterize the same process, as the larger values are obtained with vulcanizates. Through the great pressure exerted during vulcanization and the depolymerization of the rubber which precedes the final polymerization, the black is wetted by the rubber more thoroughly than during the mixing process. Though the values are hardly comparable, there is an extraordinary agreement, and, moreover, the ratio of the reinforcing effects of the two types of black is approximately the same as the ratio of the heats of wetting. Further work utilizing these methods in various forms so as to permit conclusions to be drawn from thermal data as to the mechanical properties of the mix, and using other fillers, is now in progress at the physical chemical institute at Giessen. If fillers of various sorts are to be compared, such comparison must not be limited to the active surface areas, but the interfacial tension between the rubber and the filler must be taken into consideration. Finally the particle shape, in so far as it departs from a sphere, must not be ignored.

The thermodynamics of the Joule effect in rubber.—If one stretches strips of raw rubber more than 100 per cent, they become warm. This is the more remarkable as other materials, metal wire for example, cool on stretching. One can easily demonstrate this characteristic behavior of rubber by holding it to the forehead immediately after stretching. The effect is not so noticeable after the first stretching as when the sample has been stretched several times, in which case the heat is

most clearly felt. Gough and Joule were the first to study this phenomenon,¹⁶ the former with raw rubber, the latter with vulcanizates, as he was not able to reproduce the results with raw rubber. Gough observed the heat developed on stretching, and demonstrated the accompanying increase in specific gravity. Furthermore, he showed that when he placed stretched rubber in water of a higher temperature than that of the rubber, the latter contracted to its original length. If the water was colder than the rubber the elongation remained more or less permanent. Joule strove for great accuracy in his experiments, and, therefore, as we have said, used vulcanized rubber. He stretched a rubber tube by applying more and more load, and measured with a thermometer the initial cooling effect and the subsequent more conspicuous warming. In this way he obtained the rise in temperature for a given stress. Then at the suggestion of Lord Kelvin he performed what is known as the "Joule experiment:"¹⁷ A rubber tube stretched under tension contracts on warming. The anisotropy of stretched rubber has been studied by Bjerken¹⁸ and Schiller.¹⁹

Recently Hock has stimulated the further study of this phenomenon.²⁰ He froze stretched or "racked" rubber by means of liquid air, and worked it with a hammer. While unstretched rubber under these conditions shows a conchoidal fracture, racked rubber splits up into fibres. This fibrous structure is best shown by raw rubber. Yet Hock was able to show the same effect with Feuchter's diffusion rubber,²¹ and, working at lower temperatures, with vulcanized and synthetic rubber. Though the Joule heat is most clearly evident in the case of raw rubber, it is present in the other modifications too. Hock, therefore, felt justified in relating these phenomena. If only raw rubber showed the Joule effect, one might ascribe the action to its histological structure;²² but, since vulcanized, synthetic, and diffusion rubber show the same phenomenon, it seems more reasonable to suppose that Joule effect and fibrous structure are a property of the molecules or molecular aggregates common to all modifications. During elongation and the accompanying decrease in volume, the molecules become aligned and brought closer together, so that cohesive forces similar to van der Waal forces come into play. These are the cause of the heat effect. If the molecular motion in rubber is decreased by cooling, the point is reached where the internal friction becomes so great that the forces which tend to restore the molecules to their former position can no longer compete with the van der Waal forces; the molecules remain in an orderly, parallel alignment, the rubber splits in the direction of stretch, and x-ray interferences are obtained.²³ It is a process which in principle resembles crystallization. To be sure, there is no sharply fixed freezing point—raw rubber "crystallizes" at about 20°C. at the highest; vulcanized and synthetic rubber show considerably lower "freezing points." The previous history of the rubber also has an effect.²⁴ It is not quite clear whether Feuchter²⁵ considers the fibrous structure and the Joule effect as a phenomenon of molecular dimensions, or whether he considers it as attributable to the latex particle, which in that case would have to be common to all the modifications of rubber.²⁶ His theory of shell aggregation has some alluring features; for if one considers the isoprene molecules as polymerized to form spherical shells, the effects obtained on stretching are independent of the direction, corresponding to the actual behavior. If the rubber is sufficiently warm, these aggregations are perfect spheres. In the unstretched state each shell touches its neighbors at six points, where valence forces are exercised. If the shells are deformed to ellipsoids by stretching, the mass of the rubber becomes less, the shells themselves are pushed closer together, and likewise the hemispherical shells into which the original shells may be considered divided by the elongation axis. New valence, cohesion, or van der Waal forces become effective, the rubber be-

comes markedly stronger, and somewhat resembles catgut. Finally it is not swollen by the ordinary rubber solvents because of the saturation of the valence forces.

We shall now treat the Joule effect from the standpoint of the dynamics involved, and, therefore, the following three factors claim our interest:

(1) U , the change in total energy, considered positive if decreased, negative if increased;

(2) $+A$, the work done by the system, or $-A$, the work done on the system;

(3) Q , the quantity of heat apparent, which is considered positive if absorbed by the system, and negative if evolved by the system.

According to the first law of thermodynamics, these values are related as follows:

$$U = A - Q$$

The mechanical work.—In measuring the work of elongation the aim was to obtain a general idea of the relations involved, and, therefore, the experiments were

TABLE III
STRESS-STRAIN DATA OF RAW RUBBER RINGS 1.5 G. IN WEIGHT. FORCE APPLIED AT ELONGATIONS OF

No.	Max. elong. in %	14.3	50	100	150	200	300	400	500	571	600%
1	42.8	300	...								
2	45.7	280	...								
3	83	250	490	...							
4	83	280	570	...							
5	127	280	560	670	...						
6	128.5	270	540	660	...						
7	145	270	530	630	620	...					
8	153	280	500	620	590	...					
9	192	300	550	670	670	640	...				
10	200	280	540	670	680	660	...				
11	202	280	520	630	630	610	...				
12	344	280	500	600	590	570	590	...			
13	348	290	530	680	690	670	630	...			
14	350	290	570	680	700	670	630	...			
15	426	280	580	680	690	660	660	700	...		
16	435	300	540	660	670	640	630	660	...		
17	541	250	530	660	670	620	580	580	580	...	
18	542	260	530	670	660	620	570	570	570	...	
19	582	310	620	730	690	630	600	600	600	650	
20	582	290	500	610	590	540	560	570	580	590	...
21	583	340	540	660	640	600	550	550	590	600	...
22	625	450	630	710	700	680	650	670	700	700	720
23	627	360	550	680	620	590	590	590	590	600	620
24	627	230	500	610	610	570	540	560	570	580	580
25	640	320	550	670	690	670	650	680	690	680	700
Average:		292	542	659	647	627	566	611	608	629	655

more detailed and basic than may appear necessary.²⁷ The work was determined mechanically by measuring the force require to stretch raw rubber rings averaging 1.5 g. in weight. These rings had an inner circumference of 14 cm. and were died out of the unsmoked sheet described before. The forces applied were too small to permit the use of the usual Schopper machine, which is designed for vulcanized rubber, so that the more sensitive fibre tester was used. Guide rolls were attached to the clamps of the fibre tester, over which the ring to be tested was placed. The lower roll could be turned by a knob during the elongation to simulate the action of the regular testing machine with vulcanized rubber. The force was indicated by the pendulum, and the elongation by a scale attached to the lower roll and a pointer soldered to the scale and accompanying the upper roll. The values obtained, which are given in Table III, were then plotted graphically

with the ordinates the tensile, and the abscissae the elongation. The room temperature was 20–22°C., and the rate of pull 12 cm. per minute. The character of the curve changes considerably with the temperature and the rate of pull.

Figure 2 shows a characteristic picture of the behavior during the first and second elongations and contractions. During the initial pull the stress increases rapidly up to 100% elongation, for restraining forces have to be overcome which do not appear in the second elongation. This agrees with Joule's finding that very low elongations are associated with a cooling effect. When the sample is stretched 100%, it starts to flow under approximately constant load, until it is stretched 700%, the breaking point. On contraction the curve meets the abscissa at about 140% elongation, representing the sub-permanent set of the ring immediately after contraction. The area between the stretch curve and the abscissa is the work expended in the elongation (A_D in Table IV). The area between the stretch curve and the contraction curve represents the hysteresis (H_D in Table IV); and the area between the contraction curve and the abscissa is the work done by the rubber on contraction (E_D in Table IV). If one repeats the process the elongation is almost proportional to the work done (A'_D in Table IV). The hysteresis (H'_D in

Hysteresis curves of Stretched Raw Rubber

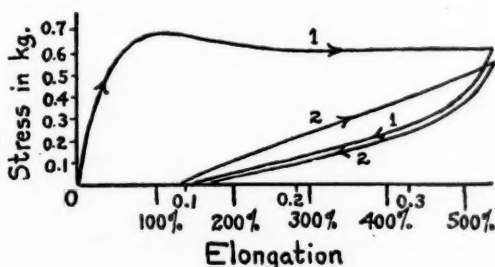


Figure 2

Table IV) is much smaller; the contraction curves lie closer together. If one repeats the process the third time, the elongation and contraction curves are approximately the same as those obtained the second time. The areas under the curves for the 25 rings given in Table III were measured with an Amler planimeter. The work values, using rings of 1.5 g. are given, in Table IV in both mechanical and calorimetric units.

The change in total energy.—From the experiments on the mechanical work it can be seen that one should not use the first elongation to measure the Joule effect, but either the first contraction or the second elongation. Yet it would be profitable to make a comparison between the first and second elongations or between the first elongation and the second contraction. Therefore an attempt was next made to measure the Joule effect directly. The experiments were carried out with rings of 0.33 g. weight, dried out of the smoked sheet described below. The method of elongation was as follows: At the end of an iron rod 70 cm. long a brass ring was fastened, there being another ring which could be moved back and forth on the rod. These rings were provided with slots so that as many as twelve rubber rings could be fastened to them. By drawing on the movable ring by means of cords, the rubber rings could be stretched. The apparatus was then

mounted in the thermostat, the calorimeter liquid being water. At the place where the iron staff projected from the water, it was covered with pieces of ivory so as to lessen heat losses. The unfavorable ratio between the large heat capacity of the calorimeter and the minimal heat effects especially at low elongations did not permit useful results.

Therefore, further work in this direction was temporarily abandoned, and the question of adiabatic elongation investigated. The heat effect was to be shown by two or three thermocouples imbedded between two rubber strips which were previously elongated. The increase in temperature was indicated by a sensitive galvanometer. From the temperature increase and the specific heat of the rubber it should be possible to calculate the Joule heat. Therefore, the specific heat had to be determined.

TABLE IV

I No.	II % Elonga- tion	III AD		IV HD		V ED		VI A'D		VII H'D	
		Kg.	G.-cal.	Kg.	G.-cal.	Kg.	G.-cal.	Kg.	G.-cal.	Kg.	G.-cal.
1	42.8	0.0108	0.0253	0.004	0.009	0.0068	0.0163	0.0088	0.0194	0.004	0.008
2	45.7	0.0114	0.0266	0.004	0.009	0.0074	0.0167	0.0102	0.0239	0.0028	0.006
3	83	0.024	0.056	0.0108	0.0253	0.0132	0.0307	0.0232	0.0543	0.010	0.0234
4	83	0.0247	0.064	0.010	0.0234	0.0237	0.0406	0.0222	0.0520	0.009	0.0210
5	127	0.0476	0.1162	0.0252	0.059	0.0224	0.0572	0.0362	0.0845	0.0152	0.0353
6	128.5	0.0478	0.1199	0.0246	0.0575	0.0232	0.0624	0.0358	0.0836	0.0154	0.0360
7	145	0.0534	0.1249	0.0308	0.0720	0.0226	0.0529	0.0322	0.0753	0.0144	0.0337
8	153	0.0536	0.1257	0.0302	0.0705	0.0234	0.0552	0.0346	0.0808	0.0144	0.0337
9	192	0.0806	0.1888	0.0524	0.1226	0.0282	0.0662	0.0418	0.098	0.0156	0.0365
10	201	0.0822	0.1924	0.0502	0.1177	0.0320	0.0744
11	202	0.0782	0.1830	0.049	0.1148	0.0292	0.0682	0.041	0.096	0.0174	0.0407
12	344	0.1324	0.310	0.094	0.250	0.0384	0.0600	0.0568	0.133	0.0282	0.0660
13	348	0.1484	0.347	0.1072	0.250	0.0412	0.0906	0.0592	0.1386	0.024	0.0560
14	350	0.1522	0.356	0.1082	0.257	0.0440	0.0930	0.060	0.1406	0.0222	0.0520
15	426	0.1898	0.444	0.142	0.332	0.0478	0.1120	0.0608	0.1422	0.0284	0.0664
16	435	0.1894	0.444	0.1416	0.331	0.0478	0.1130	0.0712	0.1669	0.0306	0.0715
17	541	0.2218	0.518	0.1646	0.385	0.0572	0.1330	0.078	0.1828	0.031	0.0725
18	542	0.2188	0.512	0.164	0.384	0.0548	0.1280	0.080	0.1871	0.0316	0.0740
19	582	0.2526	0.592	0.1894	0.442	0.0632	0.1500	0.0862	0.2019	0.039	0.0912
20	582	0.2264	0.530	0.1856	0.434	0.0408	0.0960
21	583	0.2404	0.562	0.1824	0.427	0.0580	0.1350	0.0844	0.1977	0.0336	0.0785
22	625	0.2958	0.700	0.2404	0.563	0.0554	0.1377	0.092	0.2176	0.044	0.103
23	627	0.2612	0.610	0.2032	0.475	0.0580	0.1350	0.0914	0.2138	0.0452	0.1057
24	627	0.2426	0.566	0.1910	0.446	0.0510	0.1200	0.0858	0.2008	0.0362	0.0846
25	640	0.2042	0.687	0.2326	0.543	0.0616	0.1440	0.1002	0.234	0.046	0.0178

The specific heat of raw rubber was measured by heating smooth, unsmoked sheets, obtained specially for this experiment and those following. As will be seen, the true specific heat was determined, so that the usual mixing methods were not employed in order not to heat the rubber higher than desired, and thereby introduce into the calorimeter water a rubber that was possibly different from what it was at room temperature. The following three measurements were necessary.

1. About 250 grams of rubber was rolled out with a brass mould to form a cylinder. The brass mould helped to convey the heat to the inside of the cylinder, which otherwise, due to the poor conductivity of the rubber, would not have partaken of the increase in temperature in the calorimeter when the electric current was turned on. The cylinder was lowered by means of cords into the calorimeter vessel that was filled with water. When the temperature became constant the current was turned on for 20 minutes. The relation between the galvanometer reading and the electric energy applied is given by the following equation:

$$I_1 = (G + 250x) \cdot \Delta \cdot \alpha$$

in which I_1 is the electric energy applied in calories,

G the sum of the heat capacity of the Weinhold beaker, 825 grams of water, a small rubber balloon, and 141.1 g. brass mould

x the specific heat of the raw rubber,

Δ the galvanometer reading, and

α a coefficient for the calculation of the galvanometer reading in degrees Celsius.

2. For the second determination the rubber was removed from the vessel, leaving only the 825 g. of water, the 141.1 g. of brass, and the rubber balloon, which was inflated so that its volume was the same as the rubber in the first experiment, and the height of the water in the Weinhold beaker the same as before. Otherwise the procedure was the same. This experiment can be expressed as follows:

$$I_2 = G \cdot \Delta_2 \cdot \alpha$$

where I_2 is the electric energy used in calories, Δ_2 the galvanometer reading, and G and α are the same as before.

3. In the third experiment the rubber balloon was deflated, and a volume of water added equal to that of the displaced rubber or the inflated balloon. Here we have the equation:

$$I_3 = (G + W) \cdot \Delta_3 \cdot \alpha$$

where W is the weight of the added water, and the other symbols the same as before. These three equations permit us to calculate G , α , and x .

[A representative experiment, which is described in the original with calculations and quantitative data, is omitted.—Translator.]

To be sure the large heat capacity of the Weinhold beaker as compared to that of the rubber made the results somewhat uncertain. Moreover, it was difficult to inflate the balloon to exactly the same volume as the rubber used. From three series of experiments the following values for x were obtained: 0.37, 0.40, and 0.34, so that we may say that the specific heat of raw rubber at 17° C. is 0.37.

However, let us return to the adiabatic methods. The ammeter readings were sizeable, but the variations were too large. The system was not adiabatic enough, and the ammeter too sluggish, so that the rubber cooled before a reading corresponding to the increase in temperature was shown. According to calculations from subsequent data, moderately high elongations should show a temperature increase of about 20° C., in which case the heat transfer should be quite noticeable. An approximate proportionality between the heat evolved and the elongation was evident.

On the basis of Hess' law of the conservation of heat, it was thought that unstretched rubber and rubber stretched varying amounts would attain the same status on swelling. The difference between the heats of swelling at two elongations would give the change in total energy per unit stress. Rings died out of smooth sheet and having an inner circumference of 14 cm. were stretched at 20° C. and then immediately cooled to 10° C. The chilled rings were then cut in small pieces and put in the brass cylinders to swell. Unstretched sheet gave a lower heat of swelling than crepe, as might be expected of material that differed in nature and age and therefore degree of aggregation. It may be mentioned that the rubber swelled faster the more it was stretched, due to the larger surface. Macroscopically one could distinguish three phases in rubber stretched in this way and swollen in benzene: 1, a swollen layer; 2, a layer no longer under tension but not yet

swollen; and 3, a remnant of stretched rubber in the interior of each piece, which likewise finally disappeared.

Table V gives the heat values obtained in calories per gram of rubber. The 821% elongation was obtained by dipping the ring in warm water for a moment just before stretching.

TABLE V

Elongation in per cent	0	186	361	428	621	658	821
	1.38	2.18	3.50	4.18	5.99	6.65	8.25
	1.39	2.31	3.98	4.37	8.16
	1.39
	1.48
Average	1.41	2.25	3.74	4.27	5.99	6.65	8.21

It is evident that there is a linear proportionality between the heat tone and the elongation. The theory that the Joule heat is a function of the fibre structure is confirmed by the fact that the intensity of x-ray interferences is proportional to the elongation in the same way.²⁸ According to the molecular theory of the Joule effect proposed by Hock, the Joule heat of elongation is proportional to the number of similarly oriented particles close together.

The temperature coefficient of the work of elongation.—A further result of the experiments on the mechanical work was the indication that elongation and contraction, after certain cohesive forces are first overcome, is almost a reversible process, and, if not performed too quickly, an isothermal one. Therefore, the second law of thermodynamics was applicable in the form of the Helmholtz-Gibbs equation, which includes both laws. This theory is favored by the Joule experiment, from which it follows that rubber obeys the LeChatelier-Braun principle. Therefore, the temperature coefficient of the maximal work may be obtained by corresponding experiments. Moreover, the theory requires that this quotient be positive; for, in the process of contraction, for example, the total energy increases, so that it must be taken as negative. On the other hand, the work is positive, as it is done by the system. According to the Helmholtz equation

$$\frac{dA}{dT} = \frac{A - (-U)}{T}$$

The positive coefficient may be easily explained by pointing out that it ought to be more difficult to arrange the rubber particles when the molecular motion is vigorous than when it is weak. The diminution of the volume from v_0 to v_1 , accompanying the anisotropic elongation of the rubber, requires more pull at higher temperatures. The work corresponding is

$$A = \int_{v_0}^{v_1} K \cdot dv$$

In the case of gases one can express the force as a function of v , and therefore integrate the equation, but in the case of rubber this possibility is a remote one. If one substitutes the values of A and U obtained from Tables IV and V in the above equation, then for 250, 500, and 800% elongation, there are obtained the corresponding temperature coefficients at room temperature of +0.005, +0.012 and +0.023 calories per degree Centigrade.

For experimental proof of these considerations experiments were performed which yielded a negative temperature coefficient as naturally expected by anyone acquainted with rubber. Raw rubber rings were kept overnight in a thermostat

at 21, 27, and 31° C., and stretched the next day at the same temperatures on the fibre tester previously mentioned. The work performed was determined according to the procedure described in the section on the mechanical work. The stretching was done in a small chamber that could easily be brought to the desired temperature. For elongations of 250, 500, and 800% the results gave temperature coefficients of -0.002 , -0.0024 , and -0.0035 calories per degree Centigrade, respectively.

Accordingly, the process as was expected does not fully meet the requirements of reversibility and isothermy, and, therefore, the work measured was not the maximal work. Of course, the portion of the irreversible work used to overcome the internal friction is of decisive importance, for its temperature coefficient is negative and certainly not insignificant (for example, for rape oil it is 12%). Moreover, the permanent set requires energy. There would be little satisfaction in calculating the theoretical coefficients from the three values and their temperature coefficients. It might be supposed that the part played by friction could be evaluated by carrying out the experiments at different speeds of elongation and contraction, and by extrapolating from the figures obtained the speed and also the friction. In that case, however, one would overlook the form of the energy change, which occurs principally during elongation.²⁹

In all these experiments smoked sheets were used prepared in February, 1926. In June, 1926, part was used for the experiments on the mechanical work, and in April, 1927, part for the temperature coefficients of the mechanical work. If one compares these experiments, which were ten months apart, an increase in tensile is noticeable, that is, a continuation of polymerization. Elongations of 800%, as were obtained in April, 1927, were impossible in June, 1926, as the rings broke much before this point. The figures in Table VI give a picture of the behavior.

TABLE VI

Per cent elongation	E_D	H_D		
	June, 1926	April, 1927	June, 1926	April, 1927
250	0.047	0.077	0.077	0.146
500	0.089	0.105	0.256	0.430

The symbols E_D and H_D have the same significance as in Table IV. It is obvious that the work required to produce a given elongation increases remarkably. More reliable evidence of the progress of polymerization in raw rubber may be afforded by suitable swelling experiments now in progress at this institute. From the difference in the heat of swelling of fresh and aged rubber, the degree of aggregation may be determined calorimetrically.

A contribution to the thermochemistry of vulcanization.—Vulcanization, the process which gives to rubber its resistance to mechanical and heat effects, is the alpha and omega of rubber technology. The present work was originally meant to be devoted at least partly if not wholly to this problem. There has been no lack of attempts to explain the process. During the infancy of rubber technology it was believed possible to explain it from the standpoint of pure chemistry alone and to study it exhaustively by chemical methods.³⁰ Later the physical side gained more and more consideration, so that it seems as if the physicists have won out in the race.³¹ However, few attempts of a calorimetric nature have been attempted.

Bysov,³² Kirchhof,³³ and later Perks³⁴ have taken thermometrical measurements of vulcanization processes by surrounding a thermometer with a mixture of rubber and sulfur, which was then heated in a bath. At certain temperatures they noticed a marked rise of the mercury.

In Kirchhof's experiment the calorimetric effect observed was due to secondary,

strongly exothermal reactions (combination of fillers such as litharge with sulfur). Perks followed through an extensive chemical reaction between sulfur and rubber, but not under ordinary vulcanization conditions (160° C.). Using hard rubber mixtures rich in sulfur, he observed the occurrence of a strongly exothermal reaction accompanied by the destruction of the rubber molecule (marked H₂S evolution). The much smaller heat tone of the vulcanization process itself was not determined in either case. Bysow worked on the calorimetric measurement of vulcanization, but did not obtain any significant results. As was to be expected, he obtained the same values for the heats of combustion of vulcanized and unvulcanized rubber, for the heat tone of vulcanization is but a fraction of a per cent of the comparatively enormous heat of combustion of the rubber.

These few partly unsuccessful efforts to measure the heat tone of vulcanization are an indication of the difficulties which have to be overcome, so that it does not appear strange that the section on vulcanization, which was originally meant to play the chief role in this work, has its place allotted at the end.

It seemed most profitable first to consider the Peachey process of vulcanization. In this process the rubber is subjected to the action of hydrogen sulfide on sulfur dioxide. If the heat tone of the reaction



is subtracted from the measured heat effect, the part due to the vulcanization process is obtained.

A piece of rubber was placed in a small glass reaction vessel that could easily be lowered into the calorimeter. The vessel was then filled two-thirds with hydrogen sulfide and one-third with sulfide dioxide, or else the gases were introduced alternately. The course of the reaction was followed by means of a manometer. However, the gases reacted with each other and with the rubber so slowly that distinct, reproducible results could not be obtained.

The Peachey process was, therefore, discarded and the matter of hot vulcanization considered. To be sure, it seemed decidedly more profitable to study cold vulcanization, but at that time there was only a thermobattery available whose junctions dipped directly unprotected into the calorimeter liquid. Therefore, it could be used only in dry paraffin oil. The difficulties to be met in hot vulcanization were well known. The thermostat must be heated to 100° C. or more, and this would affect the proper operation of the galvanometer. The mixtures had to be placed in cold aluminum boxes, eventually at 0° C., and lowered into the calorimeter by means of a special apparatus. Care was taken to place the mixture in one calorimeter vessel, and in the other the same quantities of rubber, sulfur, and accelerator, so that the heat capacity of the two aluminum boxes was the same as far as contents were concerned, and therefore the cooling effect was the same on both sides on inserting them into the calorimeter. In this way one could obtain a galvanometer reading corresponding to the heat tone of vulcanization. However, when the apparatus was tested out by determining the specific heat of a few metals, it appeared faulty, making reliable results impossible.

When the insulated thermostat described in the introduction was available, and after other problems of special interest were taken care of, there was an opportunity to study cold vulcanization. After some initial failures which showed that one must eliminate the slightest trace of moisture in working with sulfur chloride, and that benzene was out of the question as a solvent, an experiment similar to the following was performed.

In one calorimeter vessel was poured 1000 cc. of a 0.66% solution of rubber in benzene, in the other the same quantity of solvent. Pipettes, which could be

closed below, dipped into both vessels, and were filled with a 4% solution of sulfur chloride in benzene, which was added in portions of 6.5 to 43 grams. After temperature equilibrium was attained, the pipettes were opened and blown out with dry air. They were then filled with the rubber solution and blown out once more, and then closed above so that they remained empty till the close of the experiment. The galvanometer showed a reading of 1.5 to 5.5 scale divisions and after 15 or 20 minutes resumed its normal position. On the basis of one gram of rubber the following heat tones in calories were obtained.

TABLE VII

S_2Cl_2 used per gram rubber	1.21	1.14	0.97	0.86	0.65	0.49	0.32	0.19
Calories	3.4	5.9	3.9	3.7	3.3	3.1	1.8	1.3

Figure 3 shows the relations graphically. The abscissae are the amounts of sulfur chloride used per gram rubber, the ordinates the calories obtained.

The curve does not give much information. It is not clear whether it illustrates adsorption or chemical union. Perhaps some measurements at extremely high and low concentrations would be required to determine this point. For a compound of the formula $(C_{10}H_{16})_2S_2Cl_2$, as found by Hinrichsen and Kindscher by other methods,³⁵ the present curve has no special significance, as it occurs much later (it should lie at about 0.51 g. S_2Cl_2). Between 0.97 and 1.14 g. sulfur chloride the curve rises suddenly; after that the heat effect does not appear to increase any more. One might assume that the rise is due to the coagulation of the rubber by the sulfur chloride, occurring at high concentrations of the latter. Unfortunately time did not permit the treatment of cold vulcanization more extensively. It would seem advisable to carry out the measurements at extremely high and low concentrations and at higher temperatures, for then in the case of simple adsorption one would obtain rather small values. The rather high boiling point of the benzene and the sulfur chloride would have permitted such experiments.

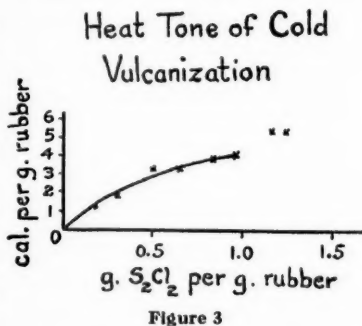


Figure 3

Conclusion

1. An apparatus is described suitable for the calorimetry of slow reactions.
2. By determining the heat of adhesion between fillers and rubber when mixed together, a method is found for the relative evaluation of technical rubber fillers. The utility of the method is shown by the comparison of the thermal data obtained using several types of black with physical data already published.
3. The elongation and contraction of raw rubber were studied from a thermodynamic standpoint, and also the change in total energy, the work of elongation, and its temperature coefficients.
4. The heat tone of the reaction between sulfur chloride and rubber dissolved in benzene was determined at a concentration of 0 to 1.3 g. of sulfur chloride to one gram of rubber. Heat tones depending on chemical and colloid-chemical processes may be exhaustively studied in this way.

References and Notes

- 1—Modeled after that of Steinwehr, *Z. phys. Chem.*, **38**, 185 (1901).
- 2—*India Rubber J.*, **60**, 379 and 423 (1920); Luff-Schmelkes, *Chemie des Kautschuks*, Berlin, **1925**, 128-141.
- 3—Luff-Schmelkes, p. 131.
- 4—North obtained the same results, *India Rubber J.*, **63**, 98.
- 5—Twiss is of the same opinion, *Ann. Rept. Appl. Chem.*, **4**, 324 (1919).
- 6—v. Hahn, *Kolloid-Z.*, **31**, 96 (1922); Leblanc, Kröger and Klotz, *Kolloidchem. Beihefte*, **20**, 356 (1925).
- 7—*Ann. chim. phys.*, **22**, 141 (1822).
- 8—*Z. angew. Chem.*, **1922**, 722.
- 9—Cf. Hock and Boström, *Gummi-Ztg.*, **1927**, No. 20.
- 10—Leblanc, Kröger and Klotz, *Kolloidchem. Beihefte*, **20** (1926).
- 11—Hock, *Kautschuk*, **1927**, 207.
- 12—Freundlich, *Kapillarchemie*, 2nd ed., 936, and Katz, *Die Gesetze der Quellung*, *Kolloidchem. Beihefte*, **9** (1917).
- 13—The heat of swelling of raw rubber is largely dependent on its condition. An article by Hock and Hartner in this connection will appear later.
- 14— $1 - (2 + 3) = 1.28 - (1.18 - 0.84) = 0.94$. This value, however, is the heat of separation of the rubber/black bond on swelling one gram of mix, and therefore is due to 0.28 g. black. One gram of black would require 3.35 calories. The heat given off to the calorimeter is taken as negative.
- 15—Foot-pounds per cubic inch = 0.01976 calories per cc. It may be pointed out here that it would be more correct to compare the resilient energy of a mix not with that of the base mix, but rather with the resilient energy of that portion of the base mix contained in it.
- 16—Joule, *Phil. Mag.*, **14**, 227 (1857); *Phil. Trans.*, **159**, 91 (1860); Gough, *Mem. Literary & Phil. Soc. Manchester*, 2nd series, vol. i, 288.
- 17—Tyndall, "Heat," **1871**.
- 18—*Ann. Phys.*, **43**, 808 (1891).
- 19—*Ann. Phys.*, **35**, 931 (1911).
- 20—*Kolloid-Z.*, **35**, 52 (1924); *Kautschuk*, 27.
- 21—*Kolloidchem. Beihefte*, **21** (1925).
- 22—Ostwald, *Kolloid-Z.*, **40**, 58 (1926); Freundlich and Hauser, *Kolloid-Z.*, **36**, 33 (1925).
- 23—Katz, *Naturwissenschaften*, **1925**, 410; *Z. Elektrochem.*, **1925**, 405; *Chem.-Ztg.*, **1927**, 53; Hauser and Mark, *Kolloidchem. Beihefte*, **22**, 63 (1926); Hock, *Kautschuk*, **1927**, 125.
- 24—Leblanc, Kröger and Klotz, *Kolloidchem. Beihefte*, **31**, 356 (1925).
- 25—*Kolloidchem. Beihefte*, **21** (1925); *Kautschuk*, Mar.-Apr., **1925**.
- 26—Ostwald, *Kolloid-Z.*, **40**, 58 (1926).
- 27—Hock and Boström, *Kautschuk*, June, **1926**.
- 28—Hauser and Mark, *Kolloidchem. Beihefte*, **22**, 63 (1926); *Ambronn-Festschrift, Kolloidchem. Beihefte*, **1926**.
- 29—Feuchter, *Kautschuk*, **1927**, No. 5.
- 30—Weber, *Z. angew. Chem.*, **112**, 142 (1894); *Kolloid-Z.*, **1**, 33 (1906); Kindscher, *Kolloid-Z.*, **8**, 245 (1911); Hinrichsen and Kindscher, *Kolloid-Z.*, **6**, 202 (1910); *Ber.*, **42**, 4329 (1909).
- 31—Leblanc and Kröger, *Kolloid-Z.*, **37**, 205; Ostwald, *Kolloid-Z.*, **6**, 137; **7**, 45 (1910); Bysow, *Kolloid-Z.*, **6**, 281 (1910); Spence and Scott, *Kolloid-Z.*, **8**, 304 (1911).
- 32—*J. Russ. Phys.-Chem. Soc.*, **1921**.
- 33—*Gummi-Ztg.*, **39**, 537, 572.
- 34—*J. Soc. Chem. Ind.*, **1926**, No. 21.
- 35—Bysow (*loc. cit.*) found that adsorption isotherms were obtained in cold vulcanization, using carbon disulfide, carbon tetrachloride, or benzene. They were not obtained with other solvents, apparently because of side reactions between the sulfur chloride and the solvent.
- 36—*Loc. cit.*

A Thermodynamic Theory of Rubber Fillers

Lothar Hock

UNIVERSITY OF GIESSEN, GERMANY
(BASED ON EXPERIMENTS BY FR. HARTNER)

Résumé

Purely thermal measurements indicate that the physical reinforcement of rubber, i. e., the increase in the work expended in rupturing, brought about by the admixture of active fillers, depends upon the free surface energy between rubber and filler, besides a work of friction, and can be measured in absolute units.

Experience has shown that the addition of so-called active fillers to rubber improves the physical properties of the latter, the work expended in breaking the rubber mixture being considerably greater than that expended in breaking the pure rubber. Furthermore, it has been found that the finer the active filler, e. g., carbon black or zinc oxide, the greater is the reinforcing effect. Obviously then the wetting of rubber and filler is the cause of the reinforcing action.

In developing from these basic principles a theory of the action of fillers, the free surface energy between rubber and filler must be considered responsible for the increased work of breaking the loaded rubber. It is desirable, therefore, to find a way to determine this free surface energy.

Now if a rubber-zinc oxide mixture is swollen in benzene, the rubber component swells and the zinc oxide is wet. This process is accompanied by a heat tone which can be measured calorimetrically, and which is not the sum of the heat of swelling of the same quantity of rubber and the heat of wetting of the zinc oxide when these are measured separately, but shows a distinctly different value. This difference represents the heat of adhesion of the filler and rubber. It also represents the total surface energy, and therefore is not a measure of the free surface energy to which is attributed the increase in the work of rupture.

Furthermore, only part of the total surface of the admixed filler comes in contact with the rubber, since wetting is incomplete because of agglomeration. The greater the concentration of the filler, the less nearly complete is this contact with the rubber. The heat of wetting per gram of filler can be determined calorimetrically for a given mixture of any concentration. This heat of wetting is a function of the concentration, and reaches its maximum value at infinite dilution of the filler, as with the molar conductivity of electrolytes in solution. This limiting value can be obtained experimentally in an approximate way by extrapolation to 0 concentration of the diminishing heats of wetting. This limiting value of the heat of wetting is designated U_0 , and it represents the heat of wetting of 1 gram of filler when every particle is completely wetted. If at a concn. c of filler the heat of wetting is U_c , the ratio U_c/U_0 is the relative extent of actual surface contact.

The calculation of the heat of wetting between rubber and carbon black in a mixture of 60% rubber and 40% active carbon black will serve as an example. From the heat of swelling of the rubber, viz., 0.1 cal. per gram, and the heat of wetting of the carbon black, viz., 2.7 cal. per gram, the heat of swelling in benzene of the mixture is calculated as 1.08 cal. per gram. However, this ignores any heat of adhesion.

On account of the surface energy between rubber and carbon black to be overcome, the observed heat of swelling was actually -0.15 cal., so that -1.23 cal. was the total surface energy. Therefore U_{40} was 3.08 cal. per g. of carbon black.

If the increase in the work of rupture brought about by addition of a filler to rubber is the free surface energy of the system, which may be designated by A , then its value may be determined by measuring the work expended in breaking the material. However, with increasing proportions of a filler which is not thoroughly mixed, a work of friction must be overcome, and this is independent of free surface energy. Here, too, the limiting value of A_0 of the ideal mixture can be obtained approximately by extrapolation of the various values of A_c to infinite dilution.

Measurements show that the order of magnitude of A_0/U_0 is 0.5 , i. e., about one-half of the calorimetrically measured total surface energy plays a part in the reinforcement of rubber by the filler. This ratio varies with the filler, and the value of 0.5 is merely an indication of the order of magnitude.

The method described makes it possible to estimate the physical properties of a mixture from a calorimetric determination of the heat of swelling. A support for the basic assumption that an increase in the work expended in rupturing is a result of the free surface energy (represented by the product of the contact surface tension δ and the surface area of contact f) may be found in the fact that its temperature coefficient (calculated with the aid of the Helmholtz-Gibbs equation from A_0 and U_0) amounts to a few tenths of one per cent, and therefore is of the same order of magnitude as the temperature coefficients of the surface tension of various other two-phase systems which have been studied experimentally. It is therefore possible in simple cases to treat on a fundamental thermodynamical basis the reinforcement of rubber mixtures.

Though the calorimetric measurement of U_0 is reliable, the dynamometric measurement of A_0 involves many difficulties of both a technical and a fundamental nature, for the reinforcement of diluted mixtures is no greater than the errors encountered in measuring the physical properties of the rubber. On the other hand, differences in the stress-strain curves of pure rubber and of loaded rubber are insignificant only at higher concentrations and activities of the filler, where the work of rupture of the pure rubber is so small compared with that of the loaded rubber that errors are of no importance.

The difficulties encountered in determining A_0 experimentally can be avoided, and it is desirable to ascertain to what successful results may be had by testing the same filler in three degrees of fineness where the relative surface areas per gram are known with some certainty. With these three rubber mixtures, there are three different values of U_0 . If f , nf , and mf represent the surface areas per gram of the three grades of filler, where only n and m must be known, and k is the fraction of U_0 which is equivalent to A_0 (in the example described above $k = 0.5$), then the three equations are: (I) $\delta f = kU_1$, (II) $\delta nf = kU_2$, (III) $\delta mf = kU_3$, in which the surface tension δ is the unknown. δ may be considered the same when the three fillers are of the same origin. If the heat tone U is expressed in absolute units, the surface tension between rubber and filler is calculated directly in dynes. The theory therefore allows the calculation of the surface tension between rubber and fillers in general. One of the equations above is sufficient for the calculation of δ , since microscopic measurements permit the determination of the absolute value of f , and k can be determined experimentally by measurement of the work of rupture A .

With reference to the calculation of U from calorimetric data, it is of importance that the smaller the heat of swelling of the rubber itself, the greater the precision of the measurement. With freshly milled raw rubber it is 0.1 cal. per gram (in

benzine), while after 9 months it is over 4 cal. This great difference is to be regarded as caused by the heat of aggregation of the rubber, and it corresponds to the increase in the work of rupture found during storage.

Swelling does not, however, break up the aggregation, and the rubber after drying and swelling again gives the same high value of the heat of swelling when it swells a second time.

By determining the factor k as well as U_0 and U_c of a given filler in the calorimetric way, and determining A_c experimentally, it is possible to estimate what proportion of the reinforcement results from the friction of the filler and what proportion results from the surface energy, i. e., what proportion of the reinforcement is of the ideal type.

Making Rubber Goods of Latex by Electro-Deposition

Paul Klein

Present manufacturing methods are characterized by repeatedly plastifying the rubber, partly by mastication and partly by heating. These operations involve the use of heavy machinery, and furthermore in certain cases the rubber mixes are then dissolved in organic solvents, a procedure which has the additional drawback of a more or less considerable loss of organic solvents.

The question at once arises: why should these many difficult and expensive steps be necessary in order to prepare a shaped body containing all the compounding and other ingredients from the original latex? There is only one answer to this question, and that is, the actual rubber manufacturer does not start with the liquid sap. Obviously it should be much easier to handle a liquid, to add to it the desired dispersed ingredients, and then to use it in some way or another to obtain the shaped article instead of performing all the masticating operations which are carried out with so much power and such heavy and expensive machinery.

But not only is this an economic question. There is more involved. The mastication of the rubber impairs its quality, and the longer the mastication of a certain mix, the poorer the physical properties of the product obtained therefrom will be.

The question why the rubber industry was built up on these lines is easily answered by the fact that latex is a colloid which is not very stable, and is very liable, during the long transport from the producing countries to the industrial countries, to undergo coagulation so that when it arrives it is more or less coagulated. It is a comparatively recent achievement to ship latex safely after preserving it with a slight, and by no means harmful, amount of ammonia. The arrival of latex as a commercial product opened up the possibility of using it as a raw material for the direct manufacture of the desired products, thus avoiding the steps of mastication and the like as used in the standard rubber industry.

In 1907, Victor Henri discovered that the rubber particles in latex carry a negative electric charge, and if placed in a substantially unidirectional electrical field, migrate to the anode. A Ceylon engineer named Cockerill attempted to use this phenomenon for producing crude rubber by electrically coagulating the particles on a metallic carrier, but it does not seem that much success was obtained by this method.

This was the starting point of the new process of electro-deposition. Now when an electric current is passed through commercial latex, different phenomena occur simultaneously. The rubber particles migrate toward the anode, and may lose their electrical charge and coagulate there. On the other hand, the electrolytes present in the serum are decomposed by the current and cause the generation of gas bubbles at the anode. If this gas generation is not avoided, or if no provision is made for the gas bubbles to escape in some way, the gas will pass into or through the fresh rubber deposit, thereby rendering it spongy, porous, and valueless for any commercial purpose. In order to be able to utilize cataphoresis as a method of forming rubber goods from latex, this difficulty had first to be overcome.

The problem has been solved in several ways. First, between the metallic

anode and the latex, a porous former was interposed, made, for instance, of porous porcelain, which would allow the passage of the electrolytes, but would withhold the relatively large rubber globuloids (see Fig. 1). An electrolyte placed between the former and the metallic electrode completed the circuit. The porous former had the shape of the desired article, and thus, by passing the current for a certain time, a homogeneous layer was deposited on the outside surface of the former, whereas the gases were liberated at the anode inside that former and escaped through the electrolyte. No damage was then incurred by the rubber deposited, and a non-porous, fully homogeneous rubber was obtained.

Means were then sought to solve the problem of obtaining homogeneous non-porous electro deposits of rubber directly on metals. This aim was accomplished

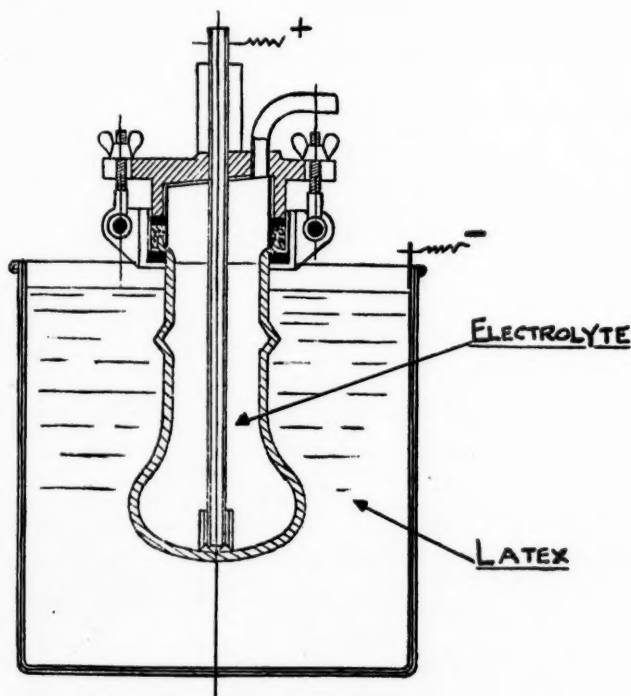


Figure 1

by working below the decomposition tension of the gas-forming electrolytes present. The cataphoretic migration occurred in practically any substantially unidirectional electrical field, whereas the electrolytical decomposition only took place when the potential difference was such that the decomposition tension of the electrolyte present was reached. By working, therefore, below the decomposition tension of the gas-forming electrolytes present, a homogeneous rubber deposit was obtained, because no gas liberation occurred at the anode to interfere with the homogeneity. The currents involved were, however, small and the method accordingly rather slow.

It was, however, possible to work above the decomposition tension of the electrolytes present and to deposit homogeneous rubber layers on metallic anodic formers. The methods which might be adopted are as follows:

(1) Add, to the latex bath, substances, the decomposition tension of which is lower than the decomposition tension of water, and which give at the anode solid anodic products instead of gases. Such electrolytes might be employed as sulfides or thiosulfates, which give sulfur, a most useful anodic product. But electrolytes producing gases at the anode may be used, if the gases are such that they will easily combine with the material of the anode. For instance, if substantial amounts of chlorides are added to latex and a zinc electrode is used, owing to the lower decomposition tension of the chlorides than that of water, chlorine will be liberated at the anode which will immediately combine with the zinc so that the deposit will again be homogeneous.

(2) Another procedure is possible. The main constituent in commercial latex causing the generation of gases is the OH ions present. If the number of OH ions be substantially diminished and electrodes are used which will, under the action of the current, continuously ionize and combine with the OH ions, there will be no liberation of gas bubbles. As anodes, zinc, cadmium or iron will serve.

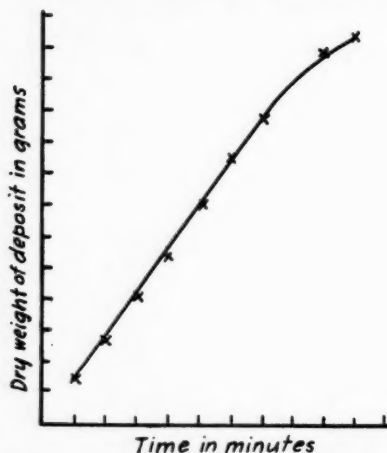


Figure 2—Amount of Rubber Deposited as a Function of the Duration

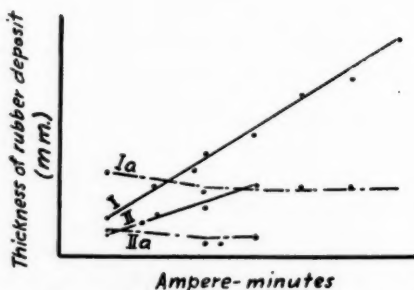


Figure 3—Rubber Deposit as a Function of the Current Density

Time of cataphoresis, 5 seconds. I. On Zn anode. II. On ceramic diaphragm. Ia. Grams of rubber deposit (on Zn) per ampere-minute. IIa. Grams of rubber deposit (on ceramic diaphragms) per ampere-minute.

As a result of these methods, a homogeneous rubber deposit instead of a spongy material may be produced.

It may appear surprising that shortly after the deposition of rubber has taken place at the anode, complete insulation does not occur, but this can be explained by the fact that in the fresh deposits the rubber globules are not packed absolutely closely, but on the contrary, these deposits contain substantial amounts of serum and form a diaphragm allowing the passage of the current. The fresh deposits are also reversible and may go in colloidal solution again if the current be reversed. They become, however, fully irreversible and insulating after drying. As a matter of fact, if the process is well conducted, the electrical resistance caused by the deposit can almost be disregarded, and substantial thicknesses may be obtained.

Figure 2 shows the thickness of the deposit as a function of the time of deposition. It can be seen that it is almost linear.

Figure 3 gives the amount of deposit as a function of the current density, and again the function is almost linear, and thus the amount of rubber deposited per ampere-minute is almost constant (Curves Ia and IIa). In this way, by varying the time for deposition or the current density, the thickness of the deposit may be regulated.

Another factor must, however, be considered, and that is the conductivity of the bath. Obviously, the greater the electrolytic conductivity of the bath the smaller will be the amount of rubber deposited by the same amount of current. Though the phenomenon of electro deposition of rubber is composed of two factors, namely, the cataphoretic migration and the coagulation of the globules at the anode, a picture may be obtained of the happenings if the first item be considered.

The speed of the cataphoretic migration is given by the formula $V = \frac{HD\xi}{4\pi\mu}$,

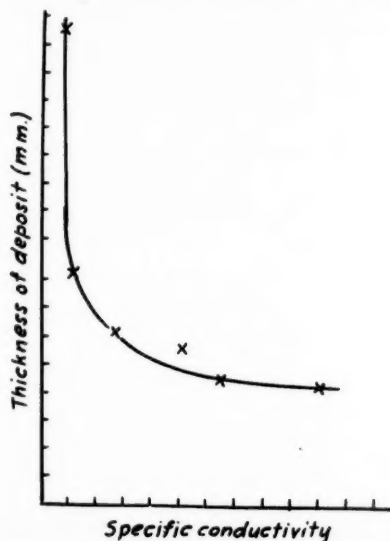


Figure 4—Thickness of Deposit from Pure Latex as a Function of Conductivity

where H is the strength of the electrical field, D the dielectric constant of the bath, ξ is the absorption potential of the dispersed particles, and μ is the internal friction of the dispersion medium. Owing to the fact that $H = A \times \frac{i}{\kappa}$ where i is the intensity of the current and κ the specific conductivity of the liquid, the above equation becomes $V = \frac{AiD\xi}{4\pi\mu\kappa}$.

From this formula it is obvious that the greater the specific conductivity κ , the smaller is the velocity of the migration. As a matter of fact, actual experiments have given the curve shown in Fig. 4, which proves that the thickness of the deposit diminishes with the increase of the conductivity.

There is another variable which must be considered, and that is the variation of the amounts deposited with the concentration of the bath. This function is given in Fig. 5, which shows that it is almost parabolic. This last curve indicates that, whereas within the limits of normal concentration, i. e., around 20 to 30 per cent,

thickness does not vary much with slight changes in the concentration, this is not the case with weaker dispersions, where the thickness of the deposit is sensitive to variations of the concentration. This leads to the necessity of keeping the concentration of the bath fairly constant. A very simple device serves for this purpose.

With a porous diaphragm, e. g., porous porcelain or asbestos board, the space between the anode and the cathode may be divided into an anodic and a cathodic compartment. The latex bath is placed in the anodic compartment, whereas a suitable electrolyte, for instance tap water, is put into the cathodic compartment. If the current be switched on, the rubber globules will migrate towards the anode and deposit there. At the same time, the separating diaphragm will cause the inverse of the cataphoretic migration, that is, electro-endosmosis. This consists in a migration of the liquid part of the bath through the diaphragm towards the cathodes. In this way, the same current which causes the anodic deposition of the rubber will also press a certain amount of the serum through the diaphragm into

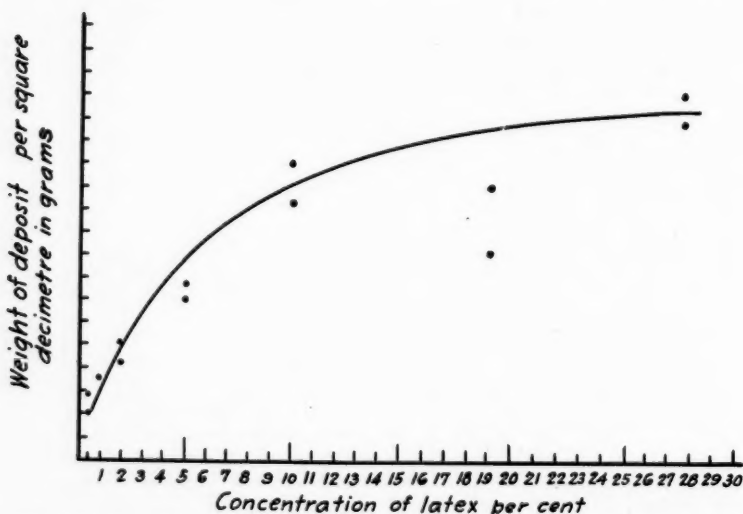


Figure 5—Quantity of Cataphoretic Deposit from Pure Latex as a Function of the Concentration of the Latex

the cathodic compartment, where it will leave the system through an overflow. In this manner, using cathode diaphragms, a means is available to keep the concentration of the bath constant. But this simple device of using cathode diaphragms bears other advantages. The physical constants of the bath, such as conductivity and the like, will thereby also be maintained practically constant.

But little would be achieved if only pure rubber could be deposited. Almost all substances in colloidal dispersion, either migrate towards the anode, or can be made to migrate in this direction. Though the speed of migration might be different from case to case, it is easy to bring about sufficiently equal migration velocities to secure fully homogeneous compounded rubber deposits. The coarser compounding ingredients are, however, preferably first disintegrated. To this effect a colloidal mill was evolved which works cheaply and efficiently and not only deflocculates as many of the mills on the market, but will also disintegrate the particles, even if they are rather coarse crystals.

This patented mill consists of a container in which small pebbles, e. g., flint stones, are moved around by a stirrer. A watery suspension of the coarse material to be disintegrated is filled into this mill. It might be interesting to note that a mill taking a charge of approximately 20 pounds of sulfur will work with only 3 horsepower, and will deliver a colloidal emulsion even of crystalline substances like sulfur, barytes and the like. For liquids and easily dispersible materials, obviously ordinary homogenizing mills may serve.

Actual experiments have shown that the composition of deposits made in production from a properly prepared mix is very constant.

The advantages of this process are that, instead of the heavy and expensive machinery of the present manufacture, only light and inexpensive machinery is needed; that the power consumption is also extremely small, the deposition of one pound of rubber, even on cathode diaphragms requiring only about 0.2 kilowatt-

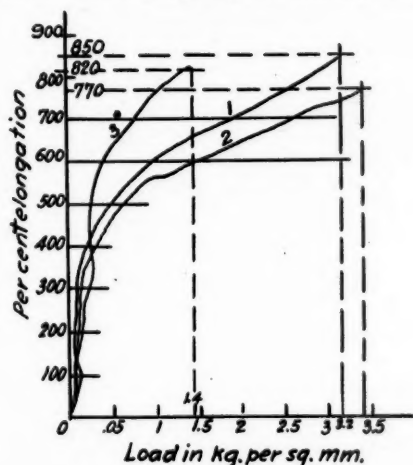


Figure 6—Stress-Strain Curve

1. Of a rubber compound made by the new process
2. Of a rubber compound made by the new process
3. Of a similar compound made by the standard process

hour; and finally that the physical properties of the product are obviously superior to those of the rubber obtained by present standard methods.

Figure 6 gives for comparison the stress-strain curves of an electro-deposited inner tube stock as against a standard inner tube stock. Tensile strengths up to 3.5 kilograms per square millimeter, with elongations of about 800 per cent are obtained, but it may be mentioned that in some cases even substantially higher figures have been reached. These high tensile strengths may be considered among other factors a consequence of the elimination of the step of masticating the rubber.

The aging of such products is also satisfactory.

A further feature of this process is that by insulating certain parts of the deposition surface, the rubber deposition only occurs on such parts of the body as desired.

In addition to these advantages, a number of articles can be made which undoubtedly would have been very difficult or almost impossible to be produced with the present process. Reference may be made in this connection to the coating of metal articles of the most various descriptions which should allow many uses of rubber, especially in the chemical industries. Owing to the fact that appropriate

rubber compounds may be evolved to resist different chemical actions, the great strength of the metal may be combined with the inactivity of the rubber. Furthermore, a good rubber is not only an anti-corrosive but an anti-abrasive, so that by covering, for instance, metal sieves, with rubber, their life will be substantially lengthened when used against loose abrasives. The insulating properties of the rubber coverings will in certain cases give an additional value.

X-Ray Contributions to the Problem of Polymerization¹

George L. Clark

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILL.

PERHAPS no subject in chemistry is so difficult, both experimentally and theoretically, or so little understood as polymerization. At the same time the phenomenon is of immeasurable importance, since rubber, cellulose, gelatin and other proteins, resins, and numerous other compounds of high molecular weight have their respective valuable properties somehow intimately based in the polymerization of relatively simple chemical substances. It is but natural, therefore, that every possible research method should be employed to answer some of the fundamental questions as to what polymerization is, when it occurs, what valence or combining forces are involved, and what the structures of these materials are. The newest of these methods is the application of x-ray diffraction by solids and liquids. It is the purpose of this paper to present the essential information which may be obtained from diffraction patterns, to outline the results of the analysis of polymerized substances, and to consider critically the general conclusions which thus far may be drawn. Two possible types of polymerization, taken in its broadest sense, are to be distinguished: (1) simple kinetic molecules associate to form a singly acting unit by the exercise of residual or secondary valence forces; and (2) monomeric molecules or residues combine with each other by the exercise of primary valence forces to form chains

¹ Presented as part of the Polymerization Symposium before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

of definite or indefinite length, as for example, in the polyoxymethylenes, $\text{—O—CH}_2\text{—(O—CH}_2\text{)—O—CH}_2\text{—}$, from formaldehyde.

Information Derived from Structure Analysis by X-Rays of Single Crystals

The x-ray analysis of crystals has essentially three phases. The first consists in the measurement of the unit crystal cell. Every crystal is built up from these ultimate units, each of which must have all the properties of the crystal itself. It is a parallelepiped whose faces are the planes of atoms which enable crystals to serve as diffraction gratings for x-rays. The cell is defined by the lengths of sides in the three directions (which are at right angles in the cubic, tetragonal, and orthorhombic systems). Now these lengths are derived simply and directly from the positions of the x-ray diffraction maxima.

Perhaps the best experimental method at the present time is the rotation method. A single crystal is mounted and rotated in a beam of monochromatic x-rays so that a principal crystallographic axis coincides with the axis of rotation. If a film is bent in a cylinder with the crystal at the center, there is registered a "layer line" diagram—that is, a series of parallel, straight, horizontal lines above and below an equatorial line, which are loci of all diffraction spots corresponding to various planes in the crystal. This pattern may now be measured so that the identity period, I , along the axis of rotation of the crystal, or in other words the edge length of the unit cell parallel to this axis, is very directly deduced from the equation $I = n \lambda / \sin \mu$, where λ is the known x-ray wave length, n is the number of the layer line from the equator (1, 2, 3, -), and μ is the angular separation measured on the film of the particular layer line from the zero equatorial line. Thus, one fundamental unit cell dimension is directly deduced independent of any assumption as to crystallographic system or positions of atoms or molecules. It may be noted that the equation is directly related to the usual Bragg diffraction equation $d = n \lambda / (2 \sin \theta)$, where θ is the angle of incidence or 2θ the angle of reflection of a beam of x-rays upon a particular set of planes. One such rotation pattern suffices to define the unit cell of a cubic crystal including its volume, the cube of an edge length. In other systems where axial ratios are not known, the crystal is oriented in one or two other directions, a pattern obtained, and measurements made of the identity periods, so that the volume of the unit cell may be calculated.

A further step may be made—namely, the deduction of the numbers of molecules of the substance in each unit cell. By "molecule" is meant the simplest formula weight expressing the chemical constitution, or the simple kinetic molecule as it is usually evident in the gaseous and liquid state. This analysis proceeds from the simple fact that the density,

ρ , of the substance under investigation which may be experimentally determined equals mass divided by volume, as follows:

$$\rho = \frac{Z M W}{V}$$

where V is the volume of the unit cell, M is the simple molecular weight, W is the weight of the hydrogen atom (1.663×10^{-24} grams) to convert mass to an absolute basis, and Z is the number of molecules each with weight M .

The foregoing direct measurements from x-ray data have given no information about the distribution of mass in the unit cell or the actual position or parameter of each of the atoms therein. These represent the further steps in the unique analysis of crystal structure. The assignment of a space group which defines the symmetry elements of the unit cell (and of the macrocrystal) follows from a consideration of crystallographic observation and etch figures and of the intensities of the x-ray diffraction maxima—i. e., presence or absence of certain planar interference maxima. The x-ray criteria for all the 230 space groups have been deduced,² together with the number of equivalent positions.

In numerous simple cases such as most of the elements, diamond, rock salt, etc., the number of atoms or molecules per unit cell deduced from densities is the same as that demanded by the space group, so that the positions of atoms are at once determined. In other cases these positions are not so simply determined and recourse must be taken to a quantitative measurement of intensities of diffraction maxima, as compared with theoretical deductions of interference based upon the laws of scattering of x-rays, in order to define uniquely the position of each atom in a unit cell of given size and space group. While this step is difficult there have been accumulated in a very few years complete analyses of several hundred crystals. It is definite knowledge now that in some cases the kinetic chemical molecule is lost sight of in the crystal building (rock salt, and similar ion-forming compounds); in other cases the single chemical molecules retain their identity in the lattice, so that forces between atoms within a molecule are greater, and distances less, than those between molecules. There is a growing list, principally from the laboratory of Sir William Bragg, of beautiful analyses of crystals of this kind, chiefly of organic compounds beginning with naphthalene and anthracene. These analyses have confirmed in a remarkable way the stereochemical conceptions upon which organic chemistry is based and have solved difficult questions of alternately possible formulas or atomic distributions—as, for example,

$(\text{NO}_2)_3 \text{ C.O.N.O.}$, instead of $(\text{NO}_2)_3 \text{ C}$, $\text{S} = \text{C} \begin{matrix} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{matrix}$ instead

² Astbury and Yardley, *Trans. Roy. Soc. London*, **234A**, 221 (1924); Wyckoff, "Analytical Expression of Results of Theory of Space-Groups," Carnegie Institute, 1922; Mark, *Ber.*, **59**, 2982 (1926); "Die Verwendung der Röntgen Strahlen in Chemie und Technik," Leipzig, 1926.

of $\text{HS}-\text{C} \begin{array}{l} \nearrow \text{NH} \\ \searrow \text{NH}_2 \end{array}$, the tetrahedral rather than pyramidal form of penta-erythritol, $\text{C}(\text{CH}_2\text{OH})_4$, etc. These studies have amply proved that the chemical molecule of benzene or of long-chain acids, or of urea, is the true building unit distributed in the unit cell.

Polymerization in Single Crystals of Pure Chemical Compounds

It so happens that for some crystalline substances the value of Z , the number of molecules determined from the volume of the unit cell and the density, is much larger than can be accommodated by the symmetry conditions of the unit cell of a given space group, even when entirely unsymmetrical molecules are assumed. The only possible interpretation of the data is, therefore, that two or more simple molecules associate or polymerize so that the aggregate acts as a unit in occupying points in the space lattice. A partial list of examples of compounds which disclose polymerization in unique x-ray diffraction analysis of single crystals is tabulated on page 289.

X-Ray Information on Solid Substances of High Molecular Weight without Single Crystals

It is evident from the foregoing discussion that the problem of unique analysis of solid structure becomes much more difficult if single crystals are not available, for the symmetry of the single crystal in large measure leads to a knowledge of the space group and the coördinates of atoms. Furthermore, the evaluation of the unit cell dimensions is not so direct, and hence accurate determinations of volume, number of chemical molecules, and polymerization number are less certain. It is this condition which must be confronted in the all-important study of the high-molecular-weight substances usually classed as polymerized and colloidal—rubber, cellulose, gelatin, fibroin, etc. In spite of this apparently discouraging outlook, it has been possible to an astonishing degree to evaluate the size of the unit crystalline cells for these materials. In the first place, these substances are all naturally fibered or may be fibered by stretching; in other words, while composed of small crystal grains, these are definitely oriented with respect to the fiber axis. When an x-ray beam passes perpendicular to the fiber a layer line pattern is produced exactly as though a single crystal were rotated around one axis. Consequently the identity period, or length of the side of the unit cell, along the axis is again directly evaluated from the simple equation $l = n\lambda / \sin \mu$. But while the single crystal may be rotated around two other axes in order to evaluate the other dimensions of the unit cell, this is impossible with the multicrystalline fiber. Recourse must now be taken to the study of the distribution of interference spots on the equator and the layer lines, in much the same way that

CRYSTALS	LATTICE	DIMENSIONS UNIT CELL (Å.)	Z	POLYMERIZATION NUMBER	AUTHORITY
Sulfur	Rhomboh	10.61 12.87 24.56	128	S_8	Bragg ¹ Mark and Wigner ⁴
Arsenious oxide	Cubic	11.06	16	(As ₂ O) ₂	Bezorth ⁵
Antimonious oxide	Cubic	11.14	16	(Sb ₂ O) ₂	Bezorth ⁵
Metalddehyde	Tetragonal	10.36 4.10	8	(CH ₃ CHO) ₄	Mark ⁴
Fumaric acid	Triclinic	7.56 (90° 40') 15.00 (88° 30') 6.20 (89° 48')	6	(C ₄ H ₂ O) ₂	Yardley ⁷
α -Quinol	Trigonal	$a = 23.07$ $c = 5.62$	18	3	Caspari ⁸
β -Quinol	Trigonal	$a = 16.25$ $c = 5.53$	9	3	Caspari ⁸
<i>m</i> -Phenylenediamine	Orthorhombic	$a = 11.97$ $b = 8.14$ $c = 23.61$	16	2	Caspari ⁸
<i>p</i> -Phenylenediamine	Monoclinic	$a = 8.29$ $b = 5.93$ $c = 24.92$ $\beta = 112^\circ 58'$	8	2	Caspari ⁸
β - <i>p</i> -Aminophenol	Orthorhombic	$a = 12.07$ $b = 11.85$ $c = 5.82$	6	3	Caspari ⁸
<i>o</i> -Nitroaniline	Orthorhombic	$a = 10.09$ $b = 20.44$ $c = 8.52$	16	4	Herrmann and Burck ¹¹

¹ "X-Rays and Crystal Structure."

⁴ *Z. physik. Chem.*, **111**, 398 (1924).

⁵ *J. Am. Chem. Soc.*, **45**, 1621 (1923).

⁷ *Ber.*, **57**, 1820 (1924); *Z. physik. Chem.*, **111**, 357 (1924).

⁸ *J. Chem. Soc.*, **127**, 2207 (1925).

⁹ *Ibid.*, **1926**, 2044.

¹⁰ *Ibid.*, **1927**, 1093.

¹¹ *Phil. Mag.*, **4**, 1276 (1927).

¹² *Z. Krist.*, **67**, 189 (1928).

the line spectra for powders are interpreted. By such methods connecting a given interference maximum with a particular set of planes in the crystals, the two other dimensions may be determined, though, of course, with much less certainty than the fiber axis identity period. At any rate the order of magnitude of these dimensions, and consequently of the unit volume, may be ascertained by comparing the number and positions of the spots lying on the equator and layer lines with those for a single crystal where the distance can be directly measured by later rotation around a new axis. In this way Mark has compared the fiber diagram of cellulose with the rotation pattern for silicon tetraphenyl around the *c* axis (6.85 Å.). The latter has many more spots on the equator and closer to the center than cellulose. This perpendicular distance, the *a* axis, for $\text{Si}(\text{C}_6\text{H}_5)_4$, determined directly from rotation around the *a* axis is 12 Å.; hence the cellulose dimension must be appreciably smaller than 12 Å. The figures in the following table represent newest and most reliable data for some of these materials.

SUBSTANCE	FIBER AXIS IDENTITY PERIOD Å.	OTHER DIMEN- SIONS Å.	VOLUME Å. ³	MOLECULES PER UNIT CELL
Rubber (stretched) ¹¹	8.1	12.3 8.3	830	(C_6H_8) ₂
Silk fibroin ¹⁴	7.0	10.4 9.27	675	Only 1 of 10 or more amino acids
Cellulose ¹⁵	10.25	8.65 7.8	692	($\text{C}_6\text{H}_{10}\text{O}_5$) ₄
Mercerized cellulose ¹⁵	10.00	8.90 8.02	712	($\text{C}_6\text{H}_{10}\text{O}_5$) ₄
Chitin ¹⁶	10.04	19.42 11.58	2340	18 acetyl-glucos- amine anhydride
Collagen	20.08		11,000	

The most remarkable fact about these results is that the unit cell is unexpectedly small and contains only a very few simple chemical molecules, as contrasted with the very large molecular weights determined by chemical methods and the other properties which indicate high polymerization. The writer¹² first suggested in 1926 that experiments should be tried utilizing much longer wave lengths in order to ascertain whether there are any evidences in x-ray diffraction of larger identity periods. Several experiments of this type have been performed, even with the K α -rays of potassium, 3.74 Å., with negative results. Thus x-rays indicate a very

¹¹ *Tech. Assocn. Papers*, Series X, p. 197 (1927).

¹² Meyer and Mark, *Ber.*, **61**, 1939 (1928); the writer has found from 75 measurements 8.003 ± 0.0005 Å. for the first value.

¹⁴ Brill, *Ann.*, **434**, 204 (1923); Meyer and Mark, *Ber.*, **61**, 1932 (1928); Herzog, *Helv. Chim. Acta*, **11**, 529 (1928), finds 6.96 Å. for the identity period, and molecular weights from chemical methods as small as 310.

¹⁵ Meyer and Mark, *Ber.*, **61**, 593 (1928); Sponsler and Dore, Colloid Symposium Monograph, Vol. IV, p. 174 (1926); and *J. Am. Chem. Soc.*, **50**, 1940 (1928), find 12.20 and 10.80 Å. for the last two values for cellulose and 10.30, 4.53, and 7.61 for the values for mercerized cellulose.

¹⁶ Meyer and Mark, *Ber.*, **61**, 1936 (1928).

small ultimate unit; chemical and physical experiments of other types, such as vapor pressure lowering, viscosity and diffusion coefficients, indicate very large units, built by polymerization of simple basic molecules—isoprene, C_5H_8 , in rubber; dehydrated glucose residue, $C_6H_{10}O_5$, in cellulose; and only one of ten or more possible amino acid compounds formed by hydrolysis of proteins. The significance of this discrepancy may well be sought instead of dismissing the x-ray data as valueless.

A few other facts should be noted before an attempt is made to deduce an explanation of these x-ray facts.

In most cases of swelling of these substances, and particularly in cellulose, there is no change in the unit cell dimensions. This can only mean that imbibition by the fiber takes place between crystalline particles. In other cases, as in treatment of cellulose with alkali, a change takes place accompanied by a 4 per cent expansion of the lattice. The lattice of inulin expands 11 per cent during swelling in water. During nitration, acetylation, methylation, etc., of cellulose the fiber structure is usually maintained. Stretched rubber loses its fiber pattern during swelling in organic vapors or liquids, and also by vulcanization; nitrocellulose is similarly affected by solution of camphor.¹⁷

The patterns for these high-molecular-weight substances are always less distinct and more diffuse than the interferences for single crystals. This seems to indicate that the crystal grains are in the colloidal range. The particle size may be determined by measuring the breadth of the diffraction maxima at points of half maximum intensity and applying in the formula deduced by Debye and Scherrer.¹⁸ These measurements indicate an average size of about 100–600 Å. In the case of rubber the line breadth is independent of the extent of elongation. Thus the colloidal micelle measured by x-rays contains 80,000 simple isoprene molecules. Herzog¹⁹ has proved that these dimensions for cellulose agree very exactly with the sizes deduced from colloidal-diffusion experiments and agreement between the two magnitudes for rubber is also good.

Remarkable experiments by Hess²⁰ prove that di- and tri-acetylcellulose and methylcellulose are molecularly dispersed in dilute solutions in agreement with x-ray data, while in concentrated solutions the molecular weights are high. Evidently this is not always true, however, in the case of other simple organic compounds which readily polymerize. Pummerer and Koch,²¹ in experiments which have

¹⁷ Ueda, *Z. physik. Chem.*, **133**, 350 (1928).

¹⁸ Zsigmondy, "Kolloid Chemie;" Laue, *Z. Krist.*, **64**, 115 (1926); Patterson, *Ibid.*, **66**, 637 (1928). Patterson doubts the validity of application to substances of relatively unknown crystalline form. New data bearing on rubber colloid particle size are being presented in another paper by Clark and Van Orden.

¹⁹ *Ber.*, **58**, 1254 (1925).

²⁰ *Ann.*, **448**, 99 (1926).

²¹ *Ibid.*, **438**, 294 (1924).

been difficult if not impossible to verify, have isolated crystals of rubber which have a monoclinic lattice and a unit cell containing one molecule only of isoprene.

Upon the basis of the foregoing facts the following questions may be asked:

(1) Is it impossible for the unit cell to be smaller than the molecule, or may diffraction be intramolecular in very large molecules (macromolecules)?

(2) Are the colloidal particles with which the chemist is familiar large molecules or micelles?

(3) Are the forces holding together the small unit cells indicated by x-ray data so strong, compared with the primary valences between atoms in a molecule, that in solution and dispersion phenomena the splitting of the solid does not take place down to the true micro-units, while in organic crystals such as naphthalene the forces between molecules are far smaller than within each molecule?

(4) Are very long chains of atoms or groups compatible with x-ray data indicating small values in three dimensions?

(5) Is the fact that the crystal spectrum for rubber and similar materials appears only upon stretching while cellulose produces such a spectrum without stretching to be ascribed to weaker affinities between molecules of the parent substance of an associated molecule or micelle, or to differences in dispersion?

Before considering these possibilities, a brief survey will be given of the outstanding contribution of x-ray diffraction science to the problem of polymerization.

Structures of Polymerization Products of Formaldehyde

The most brilliant and illuminating studies of polymerization phenomena by x-ray methods are those of Hengstenberg²² and of Ott,²³ utilizing polymerized products of formaldehyde prepared and studied in the laboratory of Staudinger. The great advantage of this work lies in the fact that the compounds may be synthesized at will directly from a definitely known parent substance, formaldehyde. Synthesis of cellulose from the residue $C_6H_{10}O_5$ is impossible, and it is further true that it has not been possible thus far to synthesize rubber with its characteristic physical and diffraction properties, from the polymerization of the hydrocarbon C_5H_8 .

RESULTS OF STUDY OF POLYOXYMETHYLENES—Debye-Scherrer (powder) spectrograms for all varieties, α (hydrate), β (sulfuric ester), γ (dimethyl ether), δ (C—C bonds instead of C—O) in all high degrees of polymerization are the same, the largest spacing being 3.87 Å. The end groups are without effect.

The diacetates show additional diffraction rings corresponding as orders to a large spacing. The higher the polymer the smaller are the rings and the larger the spacings, while all other rings also noted in the preceding paragraph are unchanged. The long direction of the crystals is normal to these planes of large spacing, so that the acetyl groups on the ends of the molecules form crystal layers parallel to the faces

²² *Ann. Physik*, **84**, 245 (1928).

²³ *Helv. Chim. Acta*, **11**, 300 (1928).

of the leaflets. By careful orientations of the small crystals by pressing on celluloid or by spontaneous arrangement, excellent spectrograms of the basal planes enabled calculation of the unit cells as follows:

		DIMENSIONS Å	VOLUME OF UNIT CELL Å. ³	DEN- SITY	MOL. WT.	MOLE- CULES PER UNIT CELL
9	CH ₂ O-diacetate	25.2 × 8.30 × 4.47	935	1.353	372	2
15	CH ₂ O-diacetate	36.8 × 7.89 × 4.56	1325	1.364	552	2

These, then, are unit crystal cells of pseudo-hexagonal habit, which contain as units whole molecules nine and fifteen times as long as a simple formaldehyde molecule. The size of the crystal itself is without meaning contrary to deductions with rubber and cellulose. The length of the unit cell is also the "molecular" length of the polymer itself, and the increment per CH₂O group is 1.9 Å. This length is indicated even more exactly by a consideration of high order reflections from the basal planes which give a periodicity along the long molecule corresponding to the length of 1 CH₂O group. Prins and Coster²⁴ found analogously that the 34th order reflection from the long spacing planes of palmitic acid was remarkably intense. The molecular length calculated from the first order divided by 34 gave the increment or periodicity per carbon atom.

When several diacetates are mixed together (polymerization 8 to 15) in the study of mixed crystals in the expectation that the long spacing diffraction maxima would disappear, there are found actually rings for each species present. This is taken to mean that only polymers of equal length lie side by side. With a polymerization degree of the order of 45, however, the x-ray pattern is identical with that of the highest polymers mentioned above indicating "mixed" crystals. In other words, beyond a certain polymer length in mixtures the ability to form undistorted molecular lattices is lost; the molecule cannot be recognized from x-ray data, and there remains only a lattice of CH₂O groups with irregularly distributed end groups.

Finally, an analysis of the high polymer structure is possible with the aid of layer line diagrams obtained with fiber needles. The dimensions of the hexagonal cell are $a = 7.74$, $b = 4.46$, $c = 17.35$ Å. The volume of 600 Å.³ thus contains eighteen CH₂O groups, with nine along on edge ($17.35 = 9 \times 1.93$). This periodicity is ascribed to a threefold screw axis with nine CH₂O groups to a turn. Ott gives the dimensions $7.79 \times 4.53 \times 7.02$ Å., with 8 molecules in two groups of 4 per unit cell.

From the standpoint of the general problem of polymerization the conclusions to be drawn from these remarkable studies of the polyoxymethylenes are as follows:

²⁴ *Nature*, 118, 83 (1926).

(1) A polymerized substance has its own distinctive macromolecule which is the unit in crystal formation. While this degree of polymerization is relatively small, the actual length may be directly determined from x-ray data, particularly if polar end groups (acetyl, ether, etc.) are present to form layers.

(2) Careful work discloses a periodicity along the length due to the simple parent molecule (formaldehyde).

(3) The size of colloidal micelles is determined by bundles of the long chains.

(4) Beyond certain degrees of polymerization x-ray methods do not longer enable estimations of polymer length. Independent of how long the chains may be, the pattern is the same and corresponds to some periodicity within the macromolecule (screw axis, etc.). End groups are without effect.

(5) In a more fundamental sense this means that a unit cell may contain less than 1 macromolecule, and that it may be far smaller than can be accounted for chemically. Such a polymer is therefore not an aggregate of simple molecules held together by secondary or stray valence forces, but has a macromolecule of indefinite length constructed from primary valence forces. This macromolecule may not be known in solution or vapor phases. In the present case polymerization and crystallization are simultaneous in the synthesis of the macromolecule. Johner has actually sublimed one polyoxymethylene forming the monomer formaldehyde in the vapor phase, and this has re-polymerized and recrystallized as another polyoxymethylene.

The present work indicates the phenomena only for polymerization in one direction. Further researches on the polymerization of more complicated basic substances in two or three directions will be awaited with greatest interest.

Structure of Cellulose

Upon the basis of the analysis of the polymerization products of formaldehyde, a considerable weight is given to the contention of Sponsler and Dore that cellulose (ramie fibers) is built up of parallel "endless" chains of dehydrated glucose residues along the fiber axis, with the residues connected by primary valence glucosidal linkages through oxygen bridges. These chains are held to one another laterally by secondary valences or residual force fields. This accounts for the strongly directional properties and the far greater swelling in cross section than in length; with this view Meyer and Mark²⁵ have lately agreed, though there are still discrepancies as to details of the interpretations of the x-ray data. Trillat²⁶ has been able to measure exactly on new photographs of cotton linters a spacing of 1.2 Å. which is an intramolecular periodicity due to the disposition of carbon atoms in the parent hexose groups constituting the elementary cell. Each of these chains may be considered a whole macromolecule, and the small size of the unit crystal cell may be accounted for in the same way as the high polyoxymethylenes. These considerations at once serve to redouble efforts to obtain single crystals of cellulose or its compounds following the lead of Hess,²⁷ who crystallized triacetylcellulose from tetrachloroethane. Thus

²⁵ *Ber.*, **61**, 593 (1928).

²⁶ *Comp. rend.*, **186**, 859 (1928).

²⁷ *Z. angew. Chem.*, **37**, 993 (1924).

it may be possible to prepare intermediate length chains which can be measured directly. These things serve also to redouble efforts to improve still further methods of x-ray diffraction, since only the most advanced technic enabled Hengstenberg to obtain his valuable results on the diacetates of polymerized formaldehyde.

On the other hand, objection must be taken in the case of cellulose that particle size of colloidal micelles is without significance. Unpublished researches by the present writer amply demonstrate that in regenerated cellulose two individuals may be present—that is to say, superposed diffraction maxima, corresponding to the same spacings, one broad and diffuse as though from distinctly colloidal crystals, and the other sharp due to much larger aggregates of parallel diffracting planes, depending upon conditions of dispersion and reagglomeration. These two vary in proportions, and the first decidedly in the widths, of diffraction maxima. Hence x-ray measurements of particle sizes here are distinctly significant even if in polyoxymethylenes they are not. The complete story of the ultimate constitution of cellulose is not yet told—in fact, only preliminary fragments.

Structure of Rubber

The interpretation of the structure of rubber and related materials is complicated not only by a very small unit crystal cell but also by the fact that the crystal spectrum does not appear at all until the rubber is stretched (except in "frozen" rubber). The x-ray researches of Katz, of Hauser and Mark, and of the writer on rubber, balata, and gutta-percha are sufficiently well known so that the briefest recapitulation will suffice.

Ordinary rubber crepe or smoked sheets show an "amorphous" diagram of two very broad diffuse rings corresponding to the spacings 14.88 and 6.05 Å. Experiments by the writer²⁸ with very pure extracted rubber hydrocarbon very carefully freed from solvent give the values 11.15 and 5.97 Å. In the presence of solvent vapor the former value may increase up to 14.76 Å. as a maximum.

Upon stretching above 75 per cent, crystal fiber interferences appear which yield the dimensions of the unit cell $8.1 \times 12.3 \times 8.3$ Å. and the unit formula $(C_5H_8)_n$. These interferences increase in intensity with elongation until "racked" rubber at 10,000 per cent elongation is as distinctly crystalline as any pure organic compound.

"Frozen" rubber yields Debye-Scherrer rings (small random crystals) when unstretched.

The effects of vulcanization, calendering, temperature, solvent swelling, presence of fillers, adiabatic or isothermal extension, latex from all botanical sources, etc., have been studied.

Balata and gutta-percha are crystalline in ordinary con-

²⁸ *Nature*, 120, 119 (1927).

dition and yield fiber diagrams upon stretching. The unit cell dimensions are different from rubber and probably from each other, even though the same hydrocarbon is involved.

Researches by the writer on the purest rubber hydrocarbon proved that the whole phenomenon is due to the hydrocarbon and not to proteins or impurities.

All synthetic polymerized rubber-like substances, such as polymerized isoprene, metastyrol, butadiene, and polyvinyl acetate,²⁹ produce "amorphous" patterns similar to rubber, which are retained unchanged up to the highest elongations. Katz,³⁰ however, maintains that with a pure methyl rubber two crystal interferences (only) appeared in addition to the amorphous rings. Metastyrol when stretched produces a pattern in which the amorphous ring splits into two segments in the direction perpendicular to the direction of stretching, very similar to the action of gelatin upon stretching, so that arrangement is taking place in one or two, but not in three, dimensions.

It is not the purpose, here, to survey critically all the theories of the structure of rubber which have been submitted to account chiefly for the property of elasticity since this has been recently done.³¹ Suffice it to say that the micromanipulator experiments of Freundlich and Hauser on latex particles, and fractionation experiments of Pummerer, Feuchter, and others have produced convincing evidence of the presence of two hydrocarbons in rubber, a higher and insoluble polymer and a lower soluble polymer of the same basic molecule. If the insoluble β form is responsible for the crystal interferences, then α is dissolved in it to form a one-phase system. Bary and Hauser show that the ratio $N_1\alpha/N_2\beta$, where N_1 and N_2 are the numbers of the corresponding molecules, may be changed by temperature or mechanical treatment; N_1/N_2 is small at ordinary temperatures but increases with temperature or working. Upon "freezing" and the appearance of crystal diffraction circles for unstretched rubber, β increases at the expense of α . During stretching α is squeezed out of β and these macromolecules in a sense crystallize or solidify, and produce crystalline interferences.

It may now be asked whether in rubber the concern again is with "endless" long chains as in polyoxymethylenes and probably in cellulose, with sub-multiples or identity periods accounting for the small unit cell indicated by x-ray data. In the first place there is a clear similarity between rubber and liquid crystals. By the classical work of Friedel there is shown to be an intermediate mesomorphic state between amorphous and crystalline—namely, nematic—in which molecules are aligned in the same direction but not in equidistant layers, and hence produce no x-ray diffraction effects. Lehmann and Vorländer's work on liquid crystals has demonstrated that these are formed only by long molecules in linear

²⁹ Whithy, McNally, and Gallay, *Trans. Roy. Soc. Can.*, **22**, 27 (1928).

³⁰ *Chem.-Ztg.*, **51**, 53 (1927).

³¹ Hauser, "Latex," 1927; Bary and Hauser, *Kautschuk*, **1928**, 96.

arrangement. However, the tendency to form liquid crystals does not increase indefinitely with length, but reaches an optimum value. Thus, while liquid crystals and racked rubber are in many respects analogous, they differ in that one diffracts x-ray like an amorphous liquid and the other like a sharply crystalline substance. We are led once more to the conception of a preformed very long macromolecule formed by high polymerization of a simple hydrocarbon C_6H_6 in which the links, bound by primary valence forces, lie on screw axes—and a small unit cell results. It is immaterial whether, in release from tension and return to the amorphous condition of rubber, these long molecules become coiled again, and out of parallel arrangement, or whether the two-phase system of β and α hydrocarbons again becomes a one-phase system with β swollen by α until the swinging amplitudes of the lattice points are too large for visible interference.³²

One of the most eloquent analogies to this proposed structure of rubber is found in the recent x-ray studies of the system nitrocellulose-camphor (celluloid) by Ueda.¹⁷ As crystalline camphor is added and goes into solid solution in a nitrocellulose fiber, which alone gives a beautiful fiber diffraction pattern, this disappears and an amorphous ring is formed. Upon extraction of the camphor the nitrocellulose diagram is regained. If a celluloid film is stretched, the camphor crystallizes out of solid solution and a nitrocellulose fiber diagram is formed. Substitute β and α rubber, respectively, for nitrocellulose and camphor and the phenomena are practically identical.

Polymerization of Liquids and Other Amorphous Materials

Perhaps the newest phase of the science of x-ray diffraction by materials is the interpretation of the very simple pattern obtained with liquids and gels. For several years these patterns consisting of one, two, or three broad diffuse rings were simply dismissed as being "amorphous" rings.

However, the fact that seemingly entirely amorphous materials such as liquids with their molecules in thermal agitation produced rings, even though ill-defined, intrigued a few chemists and physicists, and now their researches have proved that these diagrams are highly significant. Several theories have been suggested to account for a diffraction indicating some kind of an identity period in liquids: the regular spacing between atoms in a molecule, disproved by the fact that monoatomic liquids such as argon or mercury also produce diffraction rings; crystal fragments, or momentary lattice formation; and the now generally accepted view that the spacings corresponding to the rings measure the distance of nearest approach of molecules or aggregates. This mechanism was first rigorously deduced

³² The general picture of the nematic state and of long chain molecules has been accepted by Katz, *Ergebnisse exakten Naturwissenschaften*, **4**, 154 (1925); *Naturwissenschaften*, **14**, No. 38 (1926); and Feuchter, *Kautschuk*, **1928**, 103.

from theory by Zernicke and Prins and has had experimental verification in the hands of Raman and his associates, Katz, Stewart, and others. Raman, for example, has shown that the sharpness of the rings, as well as the spacings, is significant as bearing upon molecular symmetry and compressibility.

Keesom³³ first showed that for several liquids with small molecules, the identity period corresponding to the principal diffraction ring could be calculated from the molecular volume of the liquid, assuming close packing of spheres. Thus the

diffraction spacing a ($= \frac{7.72}{4\pi} \frac{\lambda}{\sin \theta/2}$, where λ is the wave length and θ the angle of diffraction) is equal to b ($= 1.33 \sqrt[3]{m/d}$, where m is the molecular weight and d the density).

DeSmedt³⁴ next found that this equality was not general, for with longer molecules b was greater than a . However, by using the formula $b = 1.33 \sqrt[3]{m/n.d}$, where n is a whole number representing the association or polymerization of the liquid, the two expressions could be brought into equality. Thus he found $n = 2$ for ethyl acetate, 2 for butyric acid, 3 for paraldehyde, and 3 for benzyl benzoate, in agreement with the association values determined by physical chemical methods.

Katz³⁵ in a new series of experiments announced that in many cases the diameter of the diffraction ring was the same for an unpolymerized substance and its polymerize as follows:

Styrol	$a = 5.9$	Metastyrol	$a = 5.9$
Indene	$a = 6.5$	Para-indene	$a = 6.4$
Chinese wood oil	$a = 5.6$	Polymerized	$a = 5.7$
Isoprene	$a = 6.0$	Natural rubber	$a = 6.0$
		Isoprene rubber	$a = 6.0$
Dimethylbutadiene	$a = 6.5$	Methyl rubber	$a = 6.7$
Erythrene	$a = 5.6$	Erythrene rubber	$a = 5.6$

It may be noted incidentally that the last three values afford a splendid method for identifying the source of a synthetic rubber, as Katz has pointed out.

On the other hand, Katz found the following changes during polymerization:

Ethyl cinnamate	$a = 5.9$	Polymerized	$a_1 = 12.8$
			$a_2 = 5.6$
Methylethylketone	$a = 6.5$	Polymerized	$a = 7.7$
Methyl acrylate	$a_1 = 6.9$	Polymerized	$a_1 = 8.6$
	$a_2 = 4.8$		$a_2 = 5.0$

In his original communications Katz failed to note one important fact, already observed by the writer with linseed and Chinese wood oils—namely, that upon polymerization an additional new ring of small diameter (large spacing) often appeared as a criterion. Hünemörder³⁶ observed this also

³³ *Physica*, **2**, 118 (1922).

³⁴ *Bull. Sci. acad. roy. Belg.*, **10**, 366 (1924).

³⁵ *Z. physik. Chem.*, **125**, 321 (1927); *Kautschuk*, **1927**, 215.

³⁶ *Kautschuk*, **1927**, 106.

for metastyrol. In a new and remarkable contribution, Krishnamurti³⁷ shows that in all cases where the surface tension method indicates association the inner ring is very prominent. The spacing calculated from it may be substituted for the value of $\sqrt{m/d}$ in the Ramsay-Shields equation with greatly improved results.

Here again there is occasion to wonder that highly polymerized substances give the same pattern as monomeric parent molecules, and in any case that the dimensions or distance of nearest approach are so small.

A few additional facts should be noted in this connection. Stewart and Morrow³⁸ have been able to show liquid diffraction maxima whose spacings were a linear function of the number of carbon atoms in a chain of the normal aliphatic alcohols and acids, together with other rings representing the lateral separation of chains. The long spacings were absent in the normal paraffins, showing that the end polar groups exercised a powerful influence in the longitudinal arrangement, just as was found in the crystallized polyoxymethylene diacetates and dimethyl ethers. In all cases the lateral spacings were nearly constant, as might be expected for carbon chains.

Katz has found that for complex molecules the "amorphous" spacing corresponded to that of one of the side chains alone (for example, triolein = oleic acid).

Contrary to the results of Katz,³⁹ Clark and associates⁴⁰ have found distinct though usually small differences in spacings with China wood oil and linseed oil having polymerization and drying. The following results on China wood oil were obtained by careful measurement of the photometric curves; they are expressed as percentage change related to the spacings of the raw liquid oil, calculated by the Bragg formula $n\lambda = 2d \sin \theta$:

Raw liquid	INNER RING	OUTER RING
	8.5 Å.	4.4 Å.
	Per cent	Per cent
Raw dry film (oxidation at room temperature)	+6	+1
Raw gel (heat-polymerized)	+3	+2
Oil plus turpentine	+12	+16
Same dry film	+13	+6

Changes have been observed in cumar and other resins. Shellac yields a crystalline pattern of sharp rings which disappear leaving only an "amorphous" ring when the shellac is heated to the plastic polymerized state. With nitrocellulose films producing amorphous patterns it was possible to follow swelling and shrinkage as shown by the results:

It is at once clear that these "amorphous" patterns for liquids and gels must have a valuable significance. In the last case of nitrocellulose it is not possible that the small numbers represent the size of a colloidal particle as it is known

³⁷ *Indian Jour. of Physics*, **2**, 491 (1928).

³⁸ *Phys. Rev.*, **30**, 232 (1927); **31**, 10, 174 (1928).

³⁹ *Z. physik. Chem.*, **125**, 321 (1927).

⁴⁰ *Nature*, **120**, 119 (1927).

in viscosity and diffusion experiments any more than that the small unit-cell dimensions for rubber or cellulose are

	FRESH Å.	LIGHT AGED Å.	HEAT AGED Å.
Untreated (dry)	7.18 4.02	7.17 4.05	6.98 3.92
Dry + residual solvent	9.30 4.47	9.32 4.47	7.86 4.31
Dry + oil softener	7.34 4.31	7.50 4.39	7.50 4.39

measurements of the true "endless" macromolecule of the polymer. Hence it is logical to treat these data for a sub-crystalline state of matter in the same way that those for crystalline materials have been interpreted. Further careful data like those of Stewart may show in many of these polymerized substances the true molecular lengths, although polar end groups and chains of only very moderate length may be essential.

Conclusion

It may be readily admitted that x-ray studies of the problem of polymerization are only in their beginning. Some complexities—as, for example, small unit cell dimensions—have been added, but in general a real contribution has already been made as a basis for further advances, which will come as knowledge of interpretation increases and as experimental technic improves.

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 3, page 249. March, 1929.]

Rubber Structure Research and Its Bearing on the Elastic Properties of Colloids in General¹

E. A. Hauser²

METALLGESELLSCHAFT A.G., FRANKFURT A/M, GERMANY

The results of research on the structure of rubber by the use of x-rays are discussed and effects found recently enumerated. New ideas as to the actual molecular structure of the rubber hydrocarbon are put forward and the importance of such new considerations in connection with the elastic properties of rubber is emphasized. Results obtained by the same method in the study of rubber derivatives are given to show that the difference in physical and chemical behavior of such derivatives can be traced to a change of molecular structure as shown by x-ray investigation. The bearing of the results obtained on rubber structure research on those obtained on other plastic high-molecular colloids or colloidal compounds is discussed, and finally, a new hypothesis on elasticity in general is put forward.

THE first part of the title of this paper is undoubtedly familiar to you, perhaps so familiar as to render it no longer of interest, for we have been literally swamped

¹ Received August 17, 1928. Presented before the joint session of the Divisions of Rubber and Colloid Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

² Non-resident associate professor of colloid chemistry, Massachusetts Institute of Technology.

with papers on this subject in the last years. The second part, however, may be new, although Professor Whitby in this part of the world and especially Staudinger, in the "old country," have frequently emphasized the similarities to be found in many organophilic colloids from the viewpoint of the organic chemist. The present paper, however, differs from those of these investigators in that it deals solely with colloidal interpretations, and it should differ from the first mentioned group in that it summarizes the various results and brings them into correlation, instead of adding to the number of discrepancies already existent in the literature of this special field of research.

In doing this, I hope to achieve three things. First, I should like to prove that the colloid chemist has already contributed considerably toward a closer understanding of the unique properties of rubber, although his connection with this substance is of fairly recent date, and that he therefore does not deserve the painful criticism that "he loves to ride in cars fitted with good tires, but has so far done nothing to improve them." Second, I should like to prove that Dinsmore's excellent and most valuable critical survey, as given in Philadelphia two years ago,³ was unduly harsh in its criticism of x-ray research. Third, I should like to put forward a perhaps new and somewhat revolutionary interpretation of x-ray results to prove that the structure of rubber is not unique to this substance, but is only one very pronounced example of a principle governing the structure of a large group of natural colloids.

The research on rubber structure as carried out in the last few years can be classified in three groups in regard to: (1) the isolation of two constituents of rubber; (2) the transformation of one constituent into the other; and (3) x-ray interpretation of rubber structure.

Isolation of Two Constituents of Rubber

It seems almost unnecessary to refer here to the first group, as this field has already been exhaustively covered. I should only like to remark that the terms "sol" and "gel" rubber as previously used do not seem adequate and that they should be replaced by the terms "alpha rubber" for the ether-soluble and "beta rubber" for the insoluble fraction, simply to avoid misunderstanding or discrepancies in the future. We can summarize these results as follows: The presence of two components or two groups of components of equal chemical constitution but differing in their consistency or degree of polymerization has been established. The group of more liquid consistency naturally corresponds to the less polymerized fraction of the hydrocarbon. One point, however, does deserve special attention, and that is the discussion regarding the amount of nitrogen present in rubber purified according to Pummerer's alkali method. It has been possible

³ Dinsmore, *IND. ENG. CHEM.*, **18**, 1142 (1926).

to find in recent years that, without changing the method, the amount of nitrogen still present in the purified rubber varies considerably with the age and the source of the latex. Furthermore, it has been recently ascertained that purified rubber, having been subjected to acetone extraction and then to ether diffusion, will give off the last traces of nitrogen (and oxygen previously never found) if the alpha and beta rubber are once more subjected to acetone extraction. For the sake of interest, it may be mentioned that such rubber does not cure to a soft rubber compound in the absence of accelerators, but can, although slowly, be transformed into ebonite.

Transformation of One Constituent into Another

It has been ascertained that a transformation of alpha into beta, and vice versa, can be induced by various means—for example, by heat, milling, extensive stretching, freezing, solvents, etc. Taking alpha and beta as the values of the degree of polymerization and n_1 and n_2 as the respective numbers of molecules, the proportion $n_1\alpha/n_2\beta$, will be a definition for any condition of the rubber, being very small at normal or lower temperatures and increasing through heat, working, etc. This rather simple assumption, which today can be considered to be based on sufficient data, will readily explain most of the behavior of crude rubber under various conditions or treatments, but it still seems necessary to say something as to how these two components are related to each other. Here we must admit that our knowledge is not yet sufficient to permit a definite answer. If we consider crude, unstretched rubber as a jelly—that is, a system consisting of a solution of two or more rubber polymers in each other—we have a direct analogy to the solution of a crystalloid in a solvent, the resulting system, irrespective of the number of original components present, being a single phase. Such a system should prove to be optically empty or wholly transparent. That this is true can be proved either by purifying rubber as completely as possible or, better still, by polymerizing chemically pure isoprene. Rubber, therefore, is an "isocolloid" according to Wolfgang Ostwald's terminology, representing a solid solution having the structure of the solid substance (beta) which is swollen by a liquid (alpha) in a manner similar to gelatin swollen by water. This conception is important in regard to the explanation of elasticity, since the converse possibility, which was once favored, would not cause elasticity. (A solid suspension in a liquid will not make this liquid elastic.)

X-Ray Interpretation of Rubber Structure

Undoubtedly the most important work, and certainly the greatest amount, has been done in x-ray research. Without discussing all the details of previous research, I will limit myself to summarizing the different conceptions as

to the cause of the appearance of interference spots when stressing rubber. Whereas Katz in his first publications assumed some kind of "crystallization" during stretch, Mark and I favored the idea that the molecular aggregates are preformed but in a swollen condition and therefore not suitable for x-ray interference, but that, by stretching, the negative internal pressure will expel the alpha rubber, thus allowing the appearance of definite interferences and at the same time changing the rubber from a jelly into a gel or, in other words, into a two-phase system.

I will now say a few words concerning the discrepancies mentioned by Dinsmore and others. These discrepancies show up especially in their calculation of the volume of a simple isoprene molecule from the figures for the unit cell volume. Such deductions are bound to be inaccurate, since such a simple calculation does not account for the intermolecular spacing and the assumptions made in calculating a unit cell volume. The unit cell volume is the result of a multiplication of the a , b , and c axes, the last one being the fiber axis. We are therefore assuming that the unit cell is represented by a crystal of cubic, orthorhombic or rhombic symmetry, but we have no real means to prove such an assumption. Furthermore, and this is the most important factor, we can only actually measure the identity period in the direction of the c axis, and the figures for a and b are again derived by simple calculation based on the so-called quadratic equation and the assumption that the crystal system is cubic, rhombic, etc., so as to allow correlation of the existing interferences in the best possible manner.

Note—Still unpublished work of Mark and Susich in Germany and Stevens and Hauser of the Massachusetts Institute of Technology (using very thin films of rubber) has shown that the identity period in the fiber axis is $8.1 \pm 0.1 \text{ \AA}$. The two other periods have been calculated by the former scientists, so $a = 12.3 \pm 0.1 \text{ \AA}$ and $b = 8.3 \pm 0.1 \text{ \AA}$. The symmetry of the unit cell which stands in best correspondence with the intensities of the interferences observed is rhombic. For further details in regard to the new indices derived at, etc., see the original papers. The amount of isoprene residues per unit cell comes very close to the Figure 8. One of the most important results of these investigations, however, is that in thin films the orientation is also perfect in the two other axes.

The diffraction of x-rays, as a whole, depends on the fact that their wave length is of the same order of magnitude as the spacing, which acts or should act as a diffraction grating. It is therefore logical to assume that the results will be the more accurate as wave lengths and spacings are more similar in dimensions. The possible error of the method, therefore, must increase with a decrease of the wave length applied and, considering all this, the results obtained in the determination of the c -identity period necessarily disagree somewhat owing to the fact that wave lengths differing from 0.718 \AA to 1.54 \AA have been used.

It is hoped that this digression has not only straightened out the reasons for these differences, but has brought us at the same time to a realization that the evaluation of a fiber

diagram is based on the determination of the identity in one direction of space, preferably in the fiber axis only, and that all the rest is simple imaginary speculation based on analogies derived from crystallographic x-ray research. There is no actual concrete unit cell in rubber and there is no "rubber crystal." These terms are simply "possibilities" and can only be of aid for further work provided we stop thinking of them as concrete individuals. They are merely geometric-crystallographic symbols.

X-ray research on cellulose, however, has carried us a considerable step further and has shown us to a maximum degree of satisfaction that this substance is built up of long chains of glucose linked together by main valency bonds, the simple glucose rings joining up to such a chain in a diagonal helix. Cohesion forces or micellar forces hold a number of these chains together, forming a bundle of parallel chains. The identity period for cellulose has been ascertained to be 10.3 Å., using Cu radiation, and Meyer and Mark have derived a model for one cellobiose molecule which exactly corresponds to this figure and at the same time explains various chemical reactions. Rubber when racked is in many of its properties closely related to fibrous materials. Can we place a whole number of isoprenes in an identity period? Assuming the C—C bond to be 1.5 Å. and the C=C to be 1.2 Å., as taken from analogous measurements, and taking the double bond as well as the pressure of methyl groups into consideration, we can do this perfectly. How must we, however, explain their disappearance in the unstretched condition? On the basis of analogy with other hydrocarbons and the peculiar tendency of racked rubber to wind back in a helix when released or heated, we may assume that the main-valency isoprene chains are a typical helix, unwinding during stretch. Mark and his co-worker, Fickentscher, have constructed a simple model, based on all our recent work, which should demonstrate this idea in a simple manner. This model will undoubtedly undergo a considerable number of changes before we can be just as satisfied with it as with the cellulose model. Nevertheless, it already allows us to visualize a number of reactions. Here again we have a multiple of such chains linking up parallel to each other and held together by cohesion, molecular forces, or secondary valencies. We can conceive that we need a certain stretch to produce a sufficient number of identity periods to obtain interference. We can imagine that a solvent or reagent will enter these parcels and loosen the micellar bonds without destroying the actual structure (topochemical reaction *f. c.* swelling of racked rubber in analogy to some reactions known in cellulose research). We can imagine that mechanical treatment will cause ruptures in the main-valency chains; that strong acids may have the same effect; the Joule effect finds a simple interpretation, as does the effect of isotropic flow. Vulcanization might find a simple explanation in the

changing of the energy ratio from the main-valency chain in the uncured in favor of the micellar bonds in the cured stock, this at the same time explaining the increase in resistance, etc., and the fact that sulfur may cause a certain amount of additional aggregation. The lack of elasticity in ebonite seems logical when we assume that we have obtained a wholly saturated system, etc. Differences in molecular weight determinations can be readily explained by assuming that the various solvents used will cause ruptures at different points, etc.

I believe, however, that we can say even more. We can postulate that all fibrous materials are built up of main-valency chains bundled together by micellar forces to form parcels of parallel chains, only the length of the chain and the number per parcel are not yet ascertainable with great accuracy. Furthermore, we can say that their elasticity will depend largely on the form of the smallest element, be it a ring as in cellulose or a straight chain as in rubber, and especially on the actual helix angle. The appearance of x-ray fiber diffraction patterns depends on the condition of these chains—i. e. whether swollen or not; for example, stretched rubber in contact with solvent vapors loosens the pattern, as do alkali-treated cellulose and celluloid. Celluloid is a perfect analogy to rubber, giving an "amorphous" scattering in unstretched condition inasmuch as the nitrocellulose has been swollen by the added camphor. Brown, however, has recently shown that celluloid when stretched sufficiently will show the original nitrocellulose pattern, the camphor having been expelled out of the fiber structure. Furthermore, with any material there is a relation between the ratio of plastic internal flow and elastic stretch. Whenever the latter can compensate the former and this state can be maintained sufficiently long, and where the viscosity of the lower polymerized phase is not such that it prevents orientation by ordinary means, thus producing an inelastic or very slightly elastic product as in the case of many resins, we will obtain a similar x-ray diffraction pattern. This has been proved by Huenemoerder with metastyrol, by Bruggmann with gelatin,⁴ and other organic jellies by Stevens, and myself on polymerized oils in work not yet published.

Conclusion

The least, therefore, to which in my opinion the colloid chemist or colloid physicist may lay claim is credit, not only for a fair contribution to the structure of rubber, but for more than that—for having laid the foundation of an entirely new conception of fibrous and elastic matter in general; this with the aid of a method, x-ray analysis, which has been so severely criticized in its connection with colloidal research. I have purposely said "foundation," because considerably more work will have to be done, and a final conception will not

⁴ Private communication.

be generally accepted until we have learned to correlate this finding with results still to be obtained in a study of double-refraction phenomena and possibly when we have learned more in regard to the interpretation of results obtained when using light of intermediate wave lengths. There is, however, nothing which should discourage us and our slogan for the purpose of increasing progress should be at all times—keep going—and how?

Note—To avoid any future dispute in regard to the two-phase theory of rubber, the author wishes to state that the two phases of the rubber hydrocarbon as revealed by chemical experiments and x-ray analysis are in themselves sufficient to produce elastic properties, the structure of the Hevea latex particle as ascertained with the micromanipulator should not be confused therewith. As this latex-particle structure in itself is a physically elastic system [see Fessenden, *J. Franklin Inst.*, **142**, 187 (1896)] we may assume that the superiority of unmilled Hevea rubber is caused by an addition of these two factors.

The author wants it, furthermore, to be understood that he does not claim a definite membrane for the Hevea particle, but a nevertheless detectable zone of a hydrocarbon of distinctly elastic properties, whereas the inside (as long as it has not come in contact with the serum or with air) is highly viscous and plastic. This zone is presumably formed by a polymerization at the interface hydrocarbon—protein containing water dispersing medium.

A New Physical Test for Vulcanized Rubber¹

D. D. Wright

HOOD RUBBER COMPANY, WATERTOWN, MASS.

This test, by use of a sample of new design, subjects rubber to a combination of tensile and shearing stresses. Shear, however, is the predominating stress. Certain aged inner tubes have been found which deteriorated more when examined by this test than a comparison of their tensile-stress-strain curves with those of fresh tubes would indicate. Tearing action seems to be approximated by this test. The effect of overcure in some cases has been recorded at earlier stages by this test than by the tensile criterion. The test is easy to perform and with usual precautions should have an accuracy of approximately 10 per cent.

VULCANIZED rubber is frequently required to withstand, not only the simple stresses such as those of compression, tensile, and shear, but also the combined effects such as torsion, tearing, bending, etc. It has been observed that, as some vulcanized rubber samples age, their resistance to shearing and tearing stresses decreases much faster than their resistance to tensile stresses, as determined under the standard procedure of rubber-testing.

During a study of natural and artificial aging some inner-tube samples, which tested very poorly after the oxygen bomb (50 hours at 60° C. and 20.4 atm.), were filed for further observation. As these tubes aged the tensile tests showed less deterioration than was expected. However, a close

¹ Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

examination of these tubes showed that they had developed a very poor resistance to tear and were weak when sudden tensile stress was applied. For sake of brevity this lack of resistance to sudden stress will be called "shortness."

After several attempts to measure this "shortness" property without resorting to some new testing machine, the tongue shear test was developed. It is so named because of the shape of the test specimen and the effect that is produced. It seems to give about the proper rating to these "short" tubes.

The Test

A specimen like that in Figure 1 is prepared by means of a cutting die, as shown by the pattern in Figure 2. Two

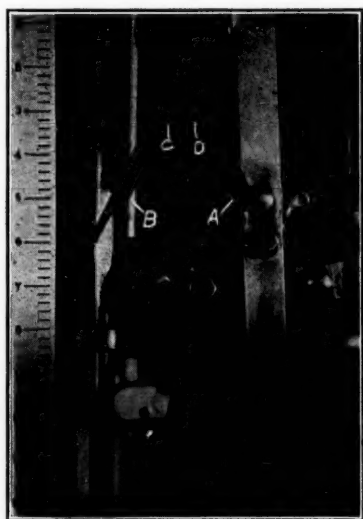


Figure 1—Test Specimen

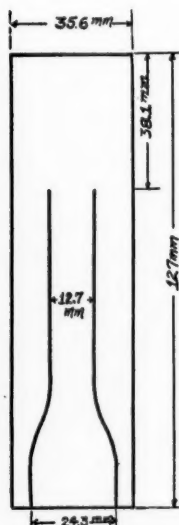


Figure 2—Pattern of Cutting Die

parallel marks exactly 1 inch (2.54 cm.) apart are placed on the test piece so that they will be near the middle of the parallel section of its tongue. The sample is then placed in the jaws of the testing machine (Figure 1). The lower jaw moves at the rate of 10 inches (25.4 cm.) per minute.

In the usual manner readings of load and elongation are taken up to and including those at rupture. From these measurements and the cross section of the tongue the shear-stress-strain curve may be plotted and the relative energy to start rupture estimated by determining the area under the curve. Figure 3 shows the comparison of the shear-stress-strain curves with the usual tensile-stress-strain curves. The reasons that the shear-stress-strain curves do not exactly coincide with the tensile-stress-strain curves seem to be:

(1) Different widths of samples were stretched; (2) different rates of stretching were employed; (3) near break certain stocks seem to yield some on shearing. In other words, the rupture is very slow while in other cases it is instantaneous. These curves are compared more fully in Table III.

A shorter and slightly less accurate method of getting the relative energy to rupture the tongue is to take one-half the product, $S \times E/100$, where S is the stress at rupture (kg. per sq. cm.) and E is the per cent ultimate elongation. The product, the "shear product," is close enough for ordinary comparisons and closer to the real energy values than the tensile product is for the relation that it expresses, because lower concavity factors exist in the shear-stress-strain curves.

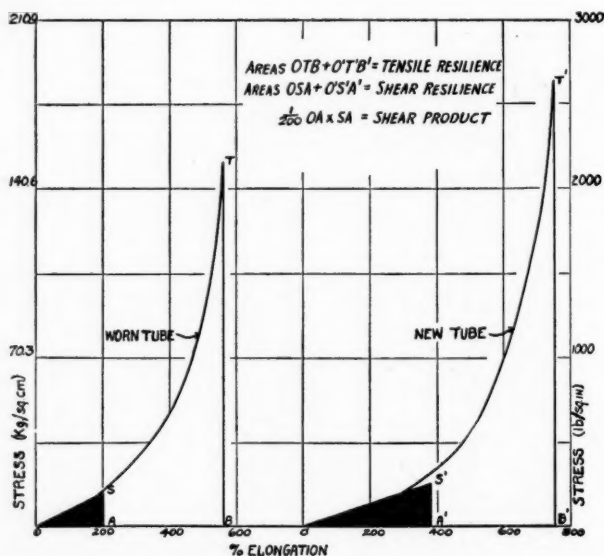


Figure 3—Stress-Strain Curves of Tongue Shear and Standard Tensile Tests

Mechanism of Test

The manner of rupture and factors influencing the values obtained were studied to learn, first, what was taking place as the rubber was strained in this sort of specimen, and second, if the test piece was properly proportioned. The rupture always takes place at the end of the tongue (C-D, Figure 1).

A much smaller expenditure of energy is required to start rupture than would be the case if the same section were broken with the standard dumbbell test specimen.

Since rubber is so elastic, the mathematical analysis of the forces that follow the straining of the tongued specimen is difficult. Therefore, the specimen shown in Figure 1 was ruled off into squares before it was put under strain in order

to present a picture of the lines of strain. As the tongue stretches out, the legs *A* and *B* twist upwards and the dips in the lines at *C* and *D* become sharper. It is evident that at these points the rubber suffers the greatest change in direction of strain and also that a marked shearing action is set up. If the cuts at *C* and *D* are rounded with a punch, ruptures are not obtained at such low energy values and the test behaves more like a tensile test.

Table I—Effect of Thickness
SHEAR TESTS

Expt.	Thickness		Plies	Shearing stress		Ultimate elongation	Shear product	
	<i>Mm.</i>	<i>In.</i>		<i>Kg./cm.²</i>	<i>Lb./in.²</i>		<i>Kg.-cm. cc.</i>	<i>In.-lbs. in.³</i>
A	0.99	0.039	1	14	203	330	24	339
	1.93	0.076	2	15	218	320	25	349
	2.94	0.116	3	23	332	410	48	680
	4.08	0.161	4	24	339	400	48	678
B	2.72	0.107	3	21	303	400	43	606
	1.83	0.072	2	22	313	360	39	556

SHEAR TESTS

Expt.	Thickness		Shearing stress		Ultimate elongation	Shear resilience	
	<i>Mm.</i>	<i>In.</i>	<i>Kg./cm.²</i>	<i>Lbs./in.²</i>	%	<i>Kg.-cm. cc.</i>	<i>In.-lbs. in.³</i>
C	0.76	0.030 ^a	10.5	152	350	18	257
	0.71	0.028 ^b	9.3	132	325	11	159
	1.40	0.055	13.5	193	375	26	364
	3.12	0.123	18.5	274	440	41	579

TENSILE TESTS

Expt.	Thickness		Tensile		Ultimate elongation	Tensile resilience	
	<i>Mm.</i>	<i>In.</i>	<i>Kg./cm.²</i>	<i>Lbs./in.²</i>	%	<i>Kg.-cm. cc.</i>	<i>In.-lb. in.³</i>
C	0.76	0.030 ^a	114	1575	740	272	3870
	0.71	0.028 ^b	98	1400	740	226	3220
	1.40	0.055	136	1900	695	306	4350
	3.12	0.123	155	2200	720	418	5950

^a Outside, next to mold face.

^b Inside, next to *a*.

Experiment A—Inner tubes of different thickness. Cured in same heat (open steam).

Experiment B—Four-ply tube buffed down.

Experiment C—Four plies of inner tube stock molded in one slab but separated with vellum to give thickness shown. Cure, 75 minutes at 141° C.

Studies of the effect of the width of the tongue and of the margin or legs outside the tongue are represented in Figures 4 and 5. These curves show that the specimen is so proportioned that it avoids the tensile effect as much as possible. The narrowing of *T* with *X* constant (Figure 4) does not produce the same type of curve as the widening of *X* with *T* constant (Figure 5). If the distribution of fiber stresses in the tongue is taken into account, this difference for tongue widths under 0.5 inch seems to be satisfactorily explained.

Various articles^{2,3,4} have shown how much tensile results are influenced by the width of the specimen. In the case of

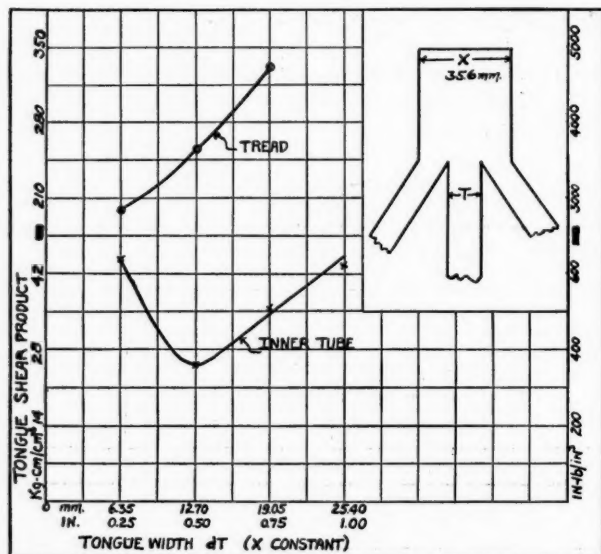


Figure 4—Effect of Width of Tongue

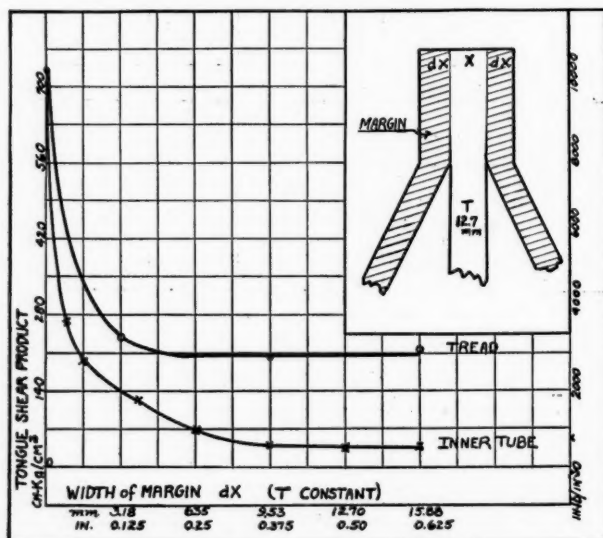


Figure 5—Effect of Margin Outside of Tongue

² Report of A. C. S. Physical Testing Committee, IND. ENG. CHEM., 17, 535 (1925).

³ Bur. Standards, Bull. 38.

⁴ Memmler and Schob, International Critical Tables, Vol. II, p. 266; Mill. Materialprüfungsamt Berlin-Dahlem, 29, 185 (1911).

Table II—Comparison of Various Stocks on Tongue Shear Test

SAMPLE	TONGUE SHEAR				STANDARD TENSILE				PAR BASIS COMPARISON	
	Stress	Ultimate elongation	Shear product	Stress	Ultimate elongation	Tensile product	Shear product	Tensile product	Shear product	Tensile product
	$\frac{Kg.}{cm.^2}$	$\frac{Lbs.}{in.^2}$	$\frac{Kg.-cm.}{cc.}$	$\frac{Kg.}{cm.^2}$	$\frac{Lbs.}{in.^2}$	$\frac{Kg.-cm.}{cc.}$	$\frac{Kg.-cm.}{cc.}$	$\frac{Lbs.-lbs.}{in.^3}$		
Carbon-black tread stock	103	1460	200	237	3370	1500	21,231	100	100	
Carbon-black tap sole	75	1067	105	134	1900	447	6,365	53	30	
Floating red tube, sp. gr. 0.98	36	505	84	201	2850	1570	22,372	42	105	
Molded tube, sp. gr. 1.28	48	682	84	274	3900	1840	26,250	26	123	
Ordinary red tube, sp. gr. 1.06	24	335	52	179	2550	1410	20,017	25	94	
Truck tube (ZnO), sp. gr. 1.44	42	590	50	239	3400	1380	19,650	92	62	
Cheap tube (whiting), sp. gr. 1.23	15	215	18.7	155	2200	924	13,112	7	26	
Black heel	34	480	40	94	1340	393	5,588	11	11	
White suede leather	202	2870	22	322	4583	160	2290	20	0	
Manila cardboard	190	2690	0.0	197	2800	0.0	0	0	

either ring or straight test pieces a decrease of width produces higher tensile values, especially on rich gum stocks. The Bureau of Standards³ shows that the more even distribution of fiber stresses in the narrow samples explains the results.

The effect of thickness is difficult to determine, because such factors as grain effect, heat lag, or heat developed while buffing the specimens may introduce serious variations. Table I shows some data obtained by three different experiments. These results leave much to be desired, but indicate that, even in the case of tensile testing of vulcanized rubber, strictly comparable results are not assured unless the specimens are of nearly the same thickness. Therefore, in performing the tongue shear test the thickness of all samples should not vary widely if comparable results are expected.

Application of Test

The tongue shear test is applicable to practically every type of soft-rubber stock produced. It suggests many interesting studies, but its most striking applications are: (a) the demonstration of the shortness property of aged inner tubes, (b) its use as a more sensitive index of the extent of artificial aging, and (c) its use with other criteria of cure or by itself to detect the beginning of overcure. Except for showing the comparison of different stocks on this test, only these three applications will be discussed.

Table III—Comparison of a Worn and a New Tube

CRITERION	EXPLANATION	UNIT	WORN TUBE A	NEW TUBE B	QUAL- ITY RATIO A/B
					%
Tensile	A. C. S. standard	Kg./cm. ²	150	176	85
		Lbs./in. ²	2130	2505	85
Resilient energy	By Sheppard's inte- gration formula	Kg.-cm./cc.	213	327	
		In.-lbs./in. ³	3024	4650	67
Tongue shear stress	(S)	Kg./cm. ²	13	18.5	
		Lbs./in. ²	186	264	70
Tongue shear strain	Ultimate elongation % (E)		190	380	50
Tongue shear resilience	From area under shear-strain curve	Kg.-cm./cc.	11	34	
		In.-lbs./in. ³	162	477	34
Tongue shear product	$\frac{1}{2}$ shear stress \times strain or $\frac{1}{2} S \times E$	Kg.-cm./cc.	12	35	
	100 or 100	In.-lbs./in. ³	176	502	35

Various kinds of stocks are compared in Figure 6 and Table II. For comparison, the carbon-black tread stock is taken as par, 100, and all other values are figured on this basis. Particular attention is called to the tread and tap sole stocks, which show very high shear resistance compared with the truck tube stock. This agrees in a general way with the tearing resistance of such stocks. In general, the effect of pigments on tear resistance is fairly well defined by the shear-product value, judging by hand-tear determinations. It has also been noted that certain accelerators give better results than others.

The sensitivity of this test to the "shortness" in some aged inner tubes is shown in Table III and Figure 3. Here a worn

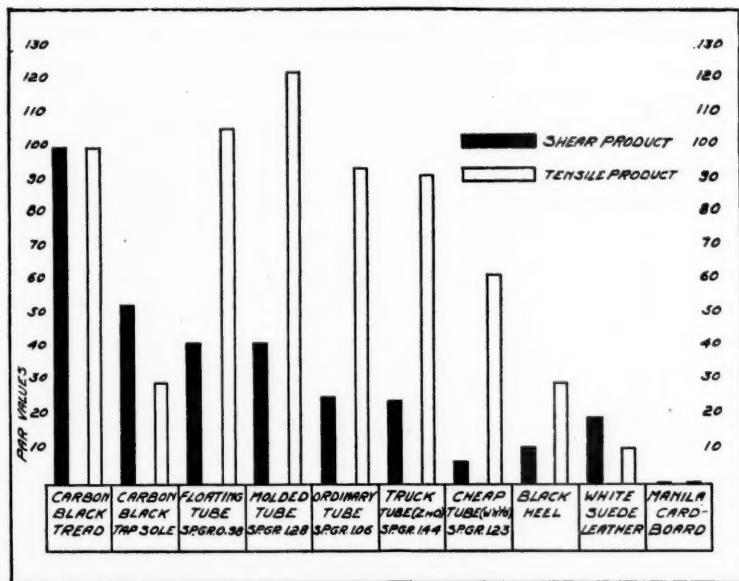


Figure 6—Comparison of Shear Product with Tensile Product on Various Stocks. Carbon-Black Tread = Par

tube is compared with a new tube compounded in nearly the same way. The worn tube had become absolutely unserviceable, yet the tensile criterion rated it 85 per cent as good as

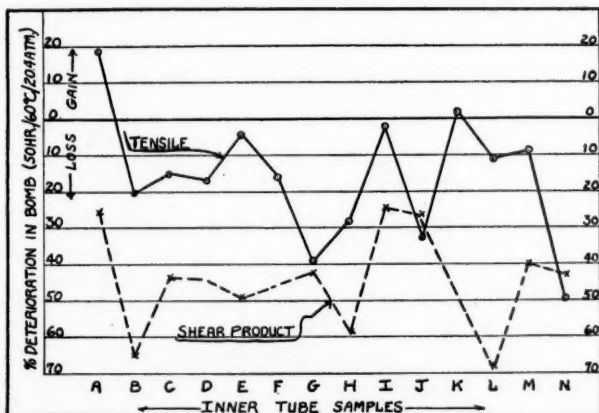


Figure 7—Effect of Bomb Aging on Tensile Strength and Shear Product

the new tube and the resilient-energy criterion, 67 per cent, while shear energy and shear product criteria rated it only 34 per cent as good. This worn tube, moreover, was very

"short" while the new tube showed no "shortness." The worn tube also showed a very weak and grainy tear. The importance of developing high-speed tensile tests or their

Table IV—Decrease of Various Criteria on Aging

TUBE	SIZE	LOSS IN BOMB AT 50 HOURS, 60° C., 20.4 ATM.		LOSS IN AIR AT 90° C., 48 HOURS	
		Tensile	Shear product	Tensile	Shear product
		%	%	%	%
A	1	+19	25	54	63
B	1	21	70	93	96
C	2	15	43	51	68
D	3	17	44	74	89
E	2	4	49	71	76
F	1	16	45	77	76
G	1	39	42	57	60
H	1	28	60	78	75
I	1	+2	24	23	11
J	1	33	27	80	65
K	4	2	50	33	73
L	4	11	69	66	78
M	4	9	40	29	70
N	1	50	43	64	64
Average		16	45	61	69

Size 1, 29 × 4.40; size 2, 31 × 5.25; size 3, 33 × 6.00; size 4, 35 × 5.

equivalents to show up this property of "shortness" in vulcanized rubber is evident.

Figure 7 and Table IV show the effect of artificial aging on the tensile and shear product values of several makes of inner tubes. The oxygen bomb test (50 hours at 60° C. and 20.4 atm.) and a 48-hour air test at 90° C. are shown. The tensile deteriorations were smaller than the shear product deteriorations in nearly every case, except in the 90° C. air test, which was so severe that tensile was reduced to about the same extent as shear product. The heat resistance of heavily pigmented tubes proves better than that of the rich gum tubes.

The sensitivity of the tongue shear test to overcure is compared with tensile and tensile product in Figure 8. No doubt there may be cases where no greater sensitivity is shown. The case

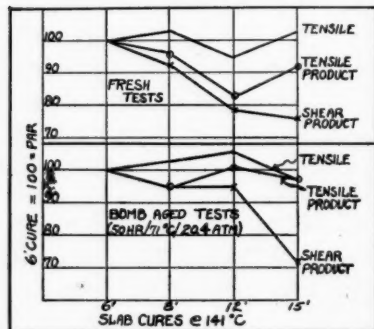


Figure 8—Shear Product vs. Tensile or Tensile Product on Overcures

given shows a tube stock cured with an ultra-accelerator. The stock showed very little decrease of tensile on long overcures. Other tests showed even the slightly overcured samples to be poor in spite of their good tensiles. On service tests tubes made from this stock developed very poor resistance

to sudden stress, weak shear resistance, and exceedingly poor tearing qualities.

Further studies of its applications are being made.

Acknowledgment

The writer wishes to express his appreciation to W. E. Glancy, N. E. Tousley, and others who have assisted so much in the perfection of this test through their helpful suggestions.

Practical Method for Obtaining Dry Air for Humidity Control in a Rubber Laboratory¹

F. S. Conover

THE NEW JERSEY ZINC COMPANY, PALMERTON, PA.

THE effect of relative humidity on rubber-testing has been the subject of much recent investigation. Stringfield² and Conover and Depew³ have published papers on this subject. The last-named authors recommended that the rubber be stored in dry cabinets before milling, between milling and vulcanization, and between vulcanization and testing, at a temperature of $75^{\circ} \pm 5^{\circ}$ F. A short time later the Physical Testing Committee of the Rubber Division of the AMERICAN CHEMICAL SOCIETY recommended that all laboratory testing be carried out at 45 per cent relative humidity and $82^{\circ} \pm 5^{\circ}$ F.

While both methods have undoubted merit, it was believed that for physical testing laboratories, particularly such as this one, zero humidity was both more conducive to reliable results and easier to maintain. Accordingly, equipment was installed for maintaining zero humidity and its performance has been consistently good. Since several of the larger rubber laboratories have shown interest in the equipment, it has been decided to present this description of the installation and its operation.

¹ Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

² IND. ENG. CHEM., **17**, 833 (1925).

³ Rubber Age, **21**, 401 (1927).

Storage Cabinets

Three storage cabinets were built. One is used for the storage of crude rubber and master batches, the second for uncured samples after milling, and the third for vulcanized samples before testing. These cabinets are ventilated by a slow stream of dry air. They are each 1.066 by 0.915 by 0.61 meters ($3\frac{1}{2}$ by 3 by 2 feet). They contain a series of 6.35-mm. ($\frac{1}{4}$ -inch) mesh wire screen shelves on which the samples and rubber are placed. (Figure 1) The air enters each box at the bottom and circulates upward and out at the top. (Figure 2)

Silica Gel Towers

In order to secure the necessary stream of dry air silica gel was used, mainly because of the ease of operation secured by this method. Silica gel is an 8- to 10-mesh silica composition

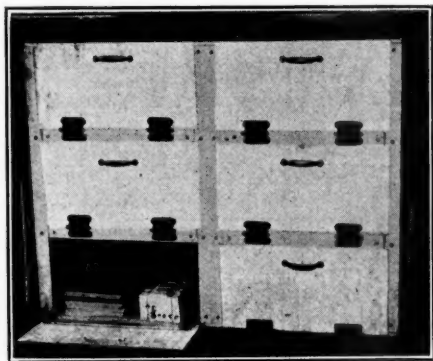


Figure 1—Storage Cabinets

having the properties of adsorbing and condensing gases at low (room) temperatures and releasing them again at high temperatures (140° to 170° C.). This property lends itself to a very convenient arrangement, for, while air is being desiccated by being passed through one dehydrator, the other dehydrator can be reactivated by heating.

Two silica gel dehydrators were built. (Figure 2) They were arranged so that one could be used to supply dry air while the other was being reactivated. Each gel tower contains 27.2 kg. (60 pounds) of silica gel, which is theoretically enough to desiccate 0.05663 cubic meter (2 cubic feet) of saturated air per minute for 4 days at 99 per cent efficiency.

Since silica gel is most efficient at low temperatures, a coil of 12.7-mm. ($\frac{1}{2}$ -inch) copper pipe was placed inside each gel tower so that water could be circulated through during the actual working periods of the apparatus.

The amount of space taken up by this equipment is small. The two towers are 0.915 meter (36 inches) high and have a

diameter of 0.3048 meter (12 inches). They are arranged side by side. A galvanized-iron tank, open at the top, was placed around them so that Sil-O-Cel could be packed between the towers and the tank to act as an insulating layer. This tank is 0.942 meter (37 inches) high, 0.509 meter (20 inches) wide, and 1.04 meters (40 inches) long.

When reactivating one of these gel towers 0.7496 cubic meter (30 cubic feet) per minute of air at 155° to 170° C. is passed through the silica gel. A large volume of air is necessary so that the material will not spoil. The air both for re-

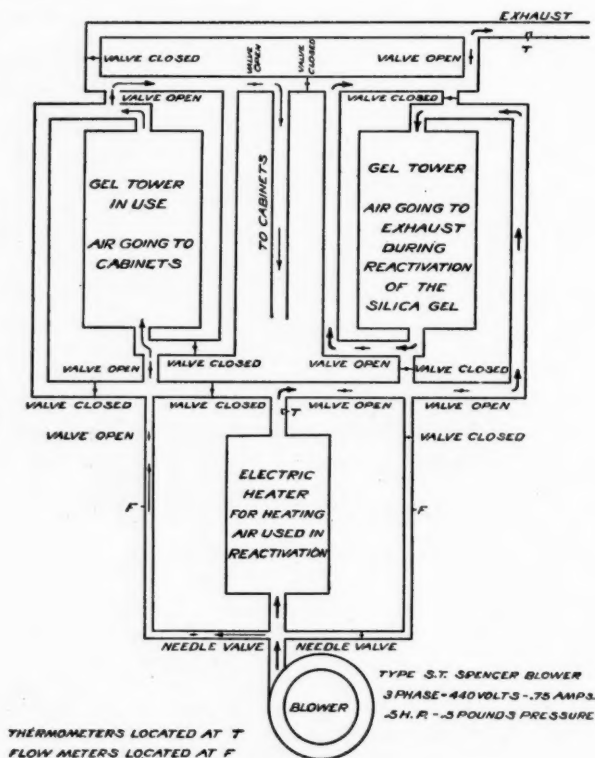


Figure 2—Diagram of Silica Gel Dehydrators

activation and dehydration is supplied by the same blower, the air for dehydration being by-passed out of the main line while the larger remaining volume goes on into the tower which is being reactivated. If the reactivation period of one tower is finished before the tower in use is exhausted, the excess air is passed out into the room. After reactivation is finished the direction of the air current is always reversed so that dehydration proceeds in the opposite direction.

Air Heaters

The air is supplied by a 5-horsepower, 3-phase, 44-volt Spencer blower which draws 0.75 ampere. The heat is supplied by six Chromolox strip heaters arranged in parallel and is regulated by means of a magnetic switch in series with a Mercoid control thermostat. (Figure 3) When the temperature of the reactivating air is too high the circuit is opened; when it is too low the circuit is closed. In this way a fairly constant temperature is maintained until the reactivating period is finished. This takes about 24 hours.

The Chromolox strip heaters are each 500-watt, 220-volt heaters (No. S-1825). The resistance of each unit is 97 ohms. The six heaters in parallel use 3 kilowatts and have a

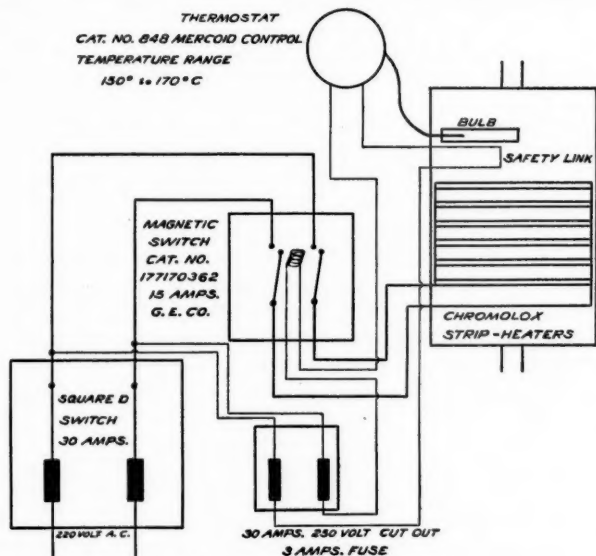


Figure 3—Diagram of Heating System

total resistance of 16.2 ohms. There are two thermometers in the system. One measures the temperature of the ingoing hot air; the other measures the temperature of the exhaust air. At the beginning of the period of reactivation the difference in temperature between the ingoing and exhaust air is about 100° C. This difference decreases very slowly until the end of the run, at which time a sharp rise in the temperature of the exhaust air is noted. After standing until cool the apparatus is ready for use.

Cost of Operation

The cost of running this equipment is low. The Spencer blower uses 580 watts at 2 cents per kilowatt-hour and the cost is \$0.0066 per hour or \$1.94 per week. Each tower requires one 24-hour reactivation period per week, making 48 hours'

work per week total, at a cost of \$2.88. The cost, then, is only \$4.82 per week for power.

During periods when the moisture content of the atmosphere is very high it is sometimes necessary to reactivate more often with a corresponding small increase in the cost of operation. Reactivation is started as soon as the relative humidity of the air, being desiccated, has passed 4 per cent.

Note—The present status of the equipment is the result of a rather long period of experimentation and growth. The reliability and accuracy of the method are shown by the fact that during September, 1928, it has been necessary to make only six reactivations in order to keep the relative humidity below 4 per cent at all times.

Humidity Readings

A pair of wet and dry bulb thermometers are placed so that small amounts of the dry air can be by-passed out and humidity readings taken from time to time. Wet and dry bulbs have sometimes been considered as rather inaccurate, especially when being used in air which is under 10 per cent relative humidity. However, the Weather Bureau of the U. S. Department of Agriculture, in a bulletin on "Psychrometry" by C. F. Marvin, asserts that this method is accurate if the velocity of the air passing the wet bulb is 4.57 meters (15 feet) per second, a condition which has been complied with in these determinations. In addition to this, gravimetric determinations using phosphorus pentoxide have been found to check the wet and dry bulbs to within 1 per cent.

Diffusion of Water through Rubber¹

Earle E. Schumacher and Lawrence Ferguson

BELL TELEPHONE LABORATORIES, 463 WEST ST., NEW YORK, N. Y.

The diffusion of water through thirteen rubbers of different compositions has been measured. The data obtained by two different methods are in satisfactory agreement.

The mathematical derivation of a simple formula for calculating the rate of diffusion has been given.

The diffusion measurements have shown: (a) that the rate of diffusion of water through a rubber membrane is inversely proportional to the square of the thickness; (b) that the rate of diffusion decreases greatly with increase in hardness; (c) that the effect of saturating the rubber with water is to increase the rate of diffusion through it, due probably not only to an increase in the water vapor pressure within the rubber, but also to a decrease in hardness; (d) that there is no intimate relationship between rate of diffusion and minor variations in the composition of the rubber.

IT HAS long been known that rubber sheets are not impervious to either gases or water. As early as 1830 J. K. Mitchell,² a Philadelphia physician, studied the problem. He and later investigators,^{3 to 6} however, were chiefly concerned

¹ Received August 18, 1928.

² *J. Med. Sci.*, **13**, 36 (1830).

³ Graham, *Phil. Mag.*, **32**, 401 (1866).

⁴ Dewar, *Proc. Roy. Inst. Gr. Brit.*, **21**, 558, 813 (1915).

⁵ Daynes, *Proc. Roy. Soc. (London)*, **97A**, 286 (1920).

⁶ Edwards and Pickering, *Chem. Met. Eng.*, **23**, 17, 71 (1920). They tested many different membranes but for all practical purposes they were very nearly alike, as their discussion shows.

with determining the relative rates of diffusion of many substances through some particular thin rubber membrane. In the present study attention has been centered on the determination of the rate of diffusion of one substance, water, through rubber of several different compositions.

Apparatus and Method

A very essential element of any diffusion-measuring apparatus is a leakproof seal between the test membrane and the chambers on each side. Preliminary work in measuring the rate of diffusion of water through various types of rubber showed that the ordinary seals using wax, cement, and similar substances probably would be satisfactory only for membranes through which diffusion is very rapid. With other membranes these sealing materials usually cause trouble by gradual crystallization and consequent leakage, evolution of gas, failure to adhere to the apparatus, or cold flow. In order to avoid these troubles a special apparatus combining a mechanical clamp and a mercury seal was developed, by means of which an air-tight chamber could be connected to each side of the test membrane. Flanges were provided on the two chambers with which to fasten the edge of the membrane, and a ball-bearing screw device clamped the parts together without any appreciable torsion on the rubber. An enclosed space about the membrane joint was filled with mercury. A detailed description of this apparatus has been published elsewhere.⁷

A thin glass capsule containing water for the test was placed in one chamber and both chambers were then evacuated to a pressure of approximately 0.01 mm. of mercury for at least 20 hours. After the capsule was broken, the amount of water which passed through the membrane was measured from time to time, either by a mercury manometer observed through a micrometer microscope or gravimetrically by observing the extension of a calibrated quartz fiber spring⁸ to which was attached a light basket containing phosphorus pentoxide. Throughout the tests the apparatus was kept in a thermostat at $25.0^{\circ} \pm 0.1^{\circ} \text{C}$.

The evacuation removed most of the sorbed gas and water from the rubber membrane and the inside of the apparatus. In the gravimetric procedure any water vapor remaining after the evacuation was absorbed by the phosphorus pentoxide before the water capsule was broken. With the manometer method the pressure indicated after the capsule was broken was the combined result of water vapor that diffused through the rubber and small amounts of residual gas and vapor gradually given off by the rubber. (Blanks and parallel tests made without breaking the capsule showed that the amounts of residual gas and vapor were small.) The magnitudes of the gas and water-vapor components were easily found by

⁷ Schumacher and Ferguson, *J. Am. Chem. Soc.*, **49**, 427 (1927).

⁸ McBain and Baker, *J. Am. Chem. Soc.*, **48**, 690 (1926).

freezing out the water vapor at -45°C . with melting monochlorobenzene while the residual gas pressure was measured. The freezing mixture reduced the vapor pressure of the water to approximately 0.06 mm. of mercury and did not appreciably affect the small pressures of carbon dioxide, sulfur dioxide, nitrogen, oxygen, and other gases likely to have been present. (The pressures of these gases were always far below those necessary to cause liquefaction at -45°C ., and only a negligible quantity could dissolve in the frozen water.)

Theoretical

DESCRIPTION OF DIFFUSION PROCESS—After the diffusion of water through rubber had been studied for some time, a general theory of the diffusion process was evolved which seems to be in agreement with the ideas of Andrews and Johnston,⁹ Lowry and Kohman,¹⁰ and others who have shown that water diffuses into rubber, is absorbed by it, and causes the rubber to swell proportionally to the amount absorbed. Most of the data included in this paper were obtained by the manometer method. Water was admitted to one side and immediately saturated that surface of the rubber. The water then began to diffuse through the rubber to the other side, so that the degree of saturation at any more remote point in the rubber increased gradually throughout the experiment. As soon as the water reached the other side of the membrane some of it evaporated, gradually building up the aqueous vapor pressure in the measuring chamber of the apparatus. The vapor pressure in the chamber was thus dependent upon the degree of saturation of the rubber at its inner surface. In many tests, even at the start, there was some water dispersed throughout the rubber so that no time was taken for the pressure to begin building up. At any stage of the test after the first increments of water reached the inner surface there was in the rubber membrane a concentration gradient varying from saturation at the reservoir side to the partial saturation at the measuring chamber side. This gradient through the membrane diminished progressively as the test proceeded.

The conditions of the tests by the gravimetric method were somewhat different. The rubber membrane was more thoroughly dried by the phosphorus pentoxide, before the test was started, than by the simple evacuation of the manometer method, and throughout the run the rubber was kept drier. The pressure head from the reservoir to the measuring chamber side of the membrane was constant throughout each experiment.

DERIVATION OF DIFFUSION FORMULA—In order to make the data obtained from the manometer tests useful in predicting the rate of diffusion of water at different humidities

⁹ *J. Am. Chem. Soc.*, **46**, 640 (1924).

¹⁰ *J. Phys. Chem.*, **31**, 23 (1927).

through rubber samples of different size and composition, some formula containing a diffusion constant had to be developed. A simple formula, based on the assumption that after water has reached the inner surface the rate at which it passes from the reservoir side of the apparatus through any particular membrane to the measuring side is proportional to the difference in vapor pressure on the two sides, was found very useful.

The assumption made was that

$$\frac{dQ}{dt} = \alpha (p_0 - p) \quad (1)$$

where Q is quantity of water vapor passing from one chamber to the other through the membrane, t is time, p_0 is the water-vapor pressure on the reservoir side of the membrane, and p is the vapor pressure on the measuring side. The rate at which water passes from one chamber to the other is proportional to A , the area of the connecting membrane. From the gas laws, the quantity of water which has passed into the measuring chamber is equal to a constant times the product of the chamber volume, V , and the vapor pressure, p , in it. Combining these proportions and proportionality constants gives

$$\frac{dp}{dt} = K (p_0 - p) \frac{A}{V} \quad (2)$$

Putting this in a form for integration,

$$\frac{dp}{(p_0 - p)} = K \frac{A}{V} dt \quad (3)$$

and the general solution is readily found to be

$$-\log_e (p_0 - p) = K \frac{A}{V} t + C \quad (4)$$

where C is the integration constant. When $t = 0$, $p = 0$, and C is thus $-\log_e p_0$. Substituting this in Equation 4 and simplifying gives the desired particular solution:

$$\log_e \left\{ \frac{p_0}{p_0 - p} \right\} = K \frac{A}{V} t \quad (5)$$

This derivation has the advantage that the assumption upon which it is based can be checked experimentally and the factors affecting the rate of diffusion can be qualitatively and quantitatively determined.¹¹

In the derivation, as seen from Equation 2, K may be considered the diffusion constant or the rate of diffusion for the membrane.

The value of K , as it stands, is affected by changes in the thickness of the sample, in its degree of saturation and aging, and in the temperature at which the test is made.

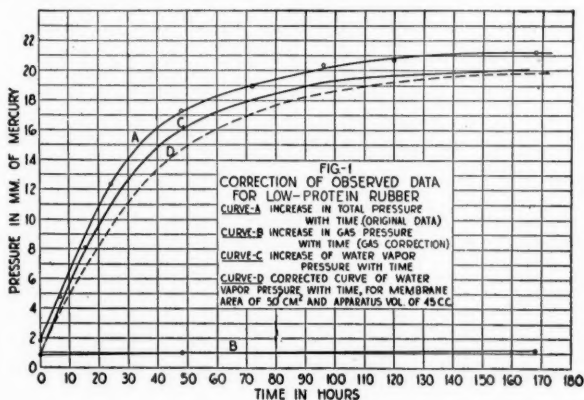
No elaborate derivation of a formula for the gravimetric data is necessary. The measurements are obtained directly in milligrams of water, W . The diffusion constant, k , in milli-

¹¹ Edwards and Pickering, *loc. cit.* They found that over the range they studied the permeability of rubber sheets to hydrogen and carbon dioxide was proportional to their partial pressure.

grams per hour for a unit membrane area and a unit pressure head, is obtained from the equation $k = \frac{W}{23.5 A t}$ in which 23.5 is the constant pressure head, A the membrane area, and t the time. The K of the manometer method and the k of the gravimetric method were compared by taking account of the gas laws and the molecular weight of water, and found to be in general agreement as illustrated by a specific instance given later.

Experimental

Before considering the experimental results, it should be stated that normally there is a characteristic variation between different samples of the same rubber which is possibly due in part to differences in the degree of aging and the extent to which the rubber was saturated with water at the outset of the experiment. For these reasons the precision of the results is not very high. On the basis of experiments per-



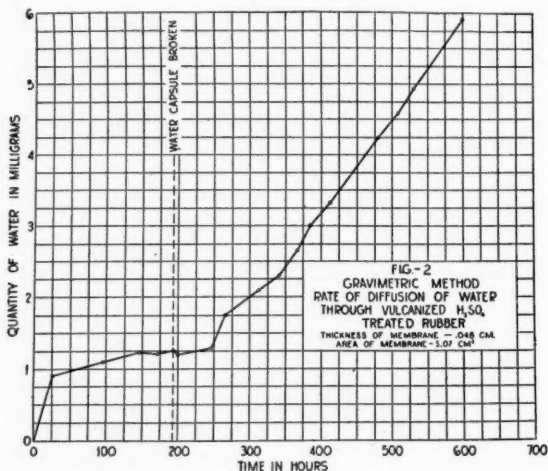
formed, it is estimated that they are reproducible only to within 10 or 15 per cent.

NATURE AND CORRECTION OF MANOMETER DATA—Since the rate of increase in pressure on the manometer side of the membrane is inversely proportional to the volume of the measuring chamber and directly proportional to the membrane area, all the measurements were corrected to a common basis of 45 cc. and 5.0 sq. cm. in order to obtain a direct comparison of the plotted results. Corrections were also applied to take care of the increase in pressure due to gases evolved by the rubber.

Curve A of Figure 1, for low-protein rubber (see list of rubber samples below) shows typical data for the increase in observed pressure with time. Curve B shows the increase of gas pressure; points on this curve represent the manometer readings when the water vapor was frozen out. The gas pressures, or ordinates of curve B, less 0.06 mm. to allow for

the vapor pressure of water at -45°C. , were subtracted from the corresponding pressures, or ordinates of curve *A*, to give curve *C*, which thus represents the increase in pressure of water vapor with time. However, since in this particular case the membrane had an area of 5.28 sq. cm. and it was tested in an apparatus of 39.0 cc. volume, the data were recalculated to the standard conditions of 45.0 cc. and 5.0 sq. cm., and plotted as curve *D*. The curves of Figure 5 were obtained in a similar way.

GRAVIMETRIC DATA—The gravimetric method of measuring the rate of diffusion was used only as a check on the manometer method. The data from a typical gravimetric test on a sheet of vulcanized sulfuric acid-treated rubber 0.048 cm. thick is shown in Figure 2. Time in hours, from the time when the apparatus was sealed off the pump, is shown plotted



against milligrams of water and the points represent actual observations. The water capsule was not broken until after 190 hours, during which time the phosphorus pentoxide absorbed the water that remained in the rubber membrane and in the apparatus (outside of the capsule) after the evacuation. When the water capsule was broken the rubber membrane must have been exceedingly dry, because it took some time for the first water to evaporate from the rubber surface in the measuring chamber.

The slope of the curve when the rate of diffusion became constant (about 150 hours after breaking the capsule) shows that 0.0135 mg. of water went through the 5.07 sq. cm. membrane every hour. The rate of passage of water through the rubber, therefore, was 0.0027 mg. per hour per sq. cm.

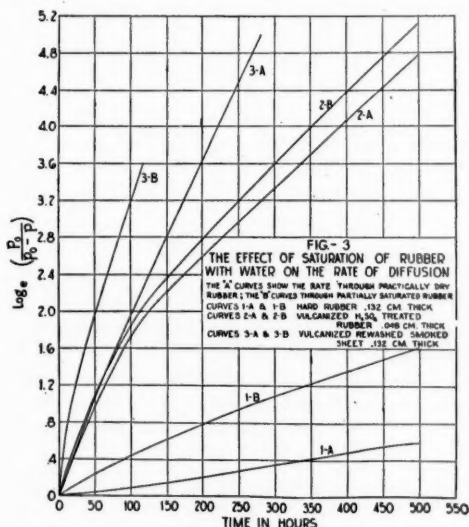
A comparison with the data taken by the manometer method can be obtained from curve *A* of Figure 4 for a sample from the same sheet of rubber. Curve *A* is plotted according

to Equation 5, and a representative slope gives a value for $K \frac{A}{V}$ of 0.0163 for a membrane area of 5.0 sq. cm. and a measuring chamber volume of 45.0 cc. From Equation 2, when $p = 0$ (the conditions of the gravimetric method),

$$\frac{dp}{dt} = K \frac{A}{V} p_0 = 0.38 \text{ mm. per hour}$$

Changing this value into milligrams per hour per square centimeter gives 0.0033 mg. The agreement with 0.0027 is satisfactory when it is remembered that the rubber membrane used in the gravimetric test was much drier and, for reasons indicated below, one would expect the diffusion to be slower.

EFFECT OF SATURATION OF RUBBER WITH WATER—Since the rate of diffusion might well be governed in part by the degree of saturation of the sample, experiments were per-



formed to determine its importance. The absorption of water by rubber increases the vapor pressure within the sheet and may produce in it a looser structure through which diffusion would be more rapid. On the other hand, the incidental swelling of the rubber globules might close up pores or capillary channels between them through which water would pass rapidly if the rubber were dry. Then, too, swelling would increase the thickness of the rubber membrane, thus increasing the diffusion path and tending to cause an apparent reduction in the rate of diffusion. The net effect of the saturation of rubber with water might be in either direction, but in all the tests made an increase in the rate of diffusion was observed.

Figure 3 shows the difference in the rate of diffusion in samples of hard rubber, vulcanized sulfuric acid-treated rubber, and vulcanized rewarmed smoked sheet at different

saturations. The curves are plotted according to Equation 5. The *A* group of curves shows the rate of diffusion during the first run on the samples when they were started from a nearly dry condition. After these runs the rubbers were allowed to become more saturated and the measuring side of the apparatus was opened and re-evacuated to 0.10 mm. for a few minutes. The tests were then continued giving the *B* group of curves, which shows that the effect of saturation is to increase the rate of diffusion.

The water evaporating into the measuring chamber during the second test could cause only a very slight decrease in the degree of saturation of the rubber membrane. The writers' experimental data and those found in the literature indicate that the saturation of the rubber changed so slowly in comparison with the time of the tests that only a negligible error was introduced.

EFFECT OF THICKNESS—To obtain a comparison of the permeabilities of the different rubbers tested, it was necessary to correct the results for the effect of sample thickness. Edwards and Pickering⁶ found the rate of diffusion of gases through rubber to be inversely proportional to the first power of the sample thickness. In the present writers' experiments the rate of diffusion was found to be approximately proportional to the square of the sample thickness. This difference is probably due to the different experimental conditions and to the much greater solubility of water in rubber than of the gases studied by Edwards and Pickering.

The relations for the problem are too complex to warrant a mathematical analysis, but the effect was studied on an empirical basis. As the test conditions were similar for all the materials, it is believed that the experimental relationship found to exist between thickness and rate of diffusion for some samples might be applied fairly to all.

Experiments were performed with three different thicknesses of vulcanized sulfuric acid-treated rubber which had given the most consistent and reproducible results in previous work. Data were obtained by the manometer method and plotted according to Equation 5, where $V = 45.0$ cc. and $A = 5.0$ sq. cm. Figure 4 shows these data, curve *A* being for a sheet 0.048 cm. thick, curve *B* for one 0.130 cm. thick, and curve *C* for one 0.279 cm. thick.

The curvature of these lines shows how difficult it is to get a good comparison of the sheets. However, an approximate average rate of diffusion can be obtained. By trial it was found that the representative slopes of these curves were inversely to each other very nearly as the squares of the thicknesses of the membranes giving them. Thus, taking the representative slope in the units of Equation 5 and the thickness in centimeters, the products of the slopes and the squares of the thicknesses for the thin, medium, and thick sheets, respectively, are 4.4×10^{-5} , 4.5×10^{-5} , and 4.7×10^{-5} .

Tests conducted with three different thicknesses of vul-

canized rewashed smoked sheet gave similar results. In general, the experiments showed the rate of diffusion of water through rubber sheets to be inversely proportional to a power of the thickness very near the second. With very thin sheets the power seemed to be smaller than for thick sheets, but in no case was it near the first power.

Types of Rubbers Tested

After the effects of saturation with water and of thickness were determined, a study of the relation of composition of the rubber to the rate of diffusion was made and the following thirteen rubbers were tested by the manometer method. The data obtained are shown graphically in Figure 5, the numbers on the curves corresponding to the numbers of the samples.

Sample 1. Vulcanized Pale Crepe—A soft rubber sheet, 0.102 cm. thick, group 4, $K' = 0.0900$

	Per cent		Per cent
Commercial pale crepe....	94.0	Zinc oxide.....	2.5
Sulfur.....	3.0	Tuads (tetramethyl thio- uramdisulfide).....	0.5

Cured 10 minutes at 130° C. Free sulfur <0.2 per cent.

Sample 2. Vulcanized Commercial Smoked Sheet—A soft rubber sheet, 0.130 cm. thick, group 4, $K' = 0.199$

	Per cent		Per cent
Commercial smoked sheet..	94.0	Tuads.....	0.5
Sulfur.....	2.5	Paraffin.....	1.0
Zinc oxide.....	2.0		

Cured 10 minutes at 130° C.

Sample 3. Vulcanized Rewashed Smoked Sheet—A soft rubber sheet, 0.130 cm. thick, group 4, $K' = 0.234$

Same as above except that rewashed smoked sheet was used instead of commercial smoked sheet.

Note—The rewashed rubber used in compounding this and other sheets was washed by a special process developed to remove the water-soluble constituents from rubber with a minimum amount of physical deterioration. The method used has been described in a footnote in a paper by Lowry and Kohman.¹⁰

Sample 4. Sulfur-Rubber Compound—A pure soft vulcanized rubber sheet, 0.114 cm. thick, group 4, $K' = 0.135$

	Per cent
Rewashed smoked sheet.....	93.0
Sulfur.....	7.0

Cured 2 hours at 140° C. This rubber was full of sulfur blotches from blooming.

Sample 5. Crude Raw Ribbed Smoked Sheet—Crude rubber as it is bought in the market, 0.280 to 0.380 cm. thick, group 5, $K' = 0.630$

Sample 6. Pure Rubber Hydrocarbon—A pure rubber hydrocarbon sheet, white in color and very tender, 0.089 cm. thick, group 5, $K' = 0.221$

Sample 7. Low-Protein Rubber—A soft vulcanized rubber sheet, 0.130 cm. thick, group 4, $K' = 0.216$

	Per cent		Per cent
Commercial pale crepe rubber steam- treated to lower protein content....	81.7	Zinc oxide.....	5.0
Sulfur.....	3.3	Paraffin.....	0.7
		Litharge.....	8.3

Cured 1 hour at 130° C. This rubber contained from 0.1 to 0.2 per cent nitrogen.

Sample 8. Sulfuric Acid-Treated Rubber¹²—An unvulcanized rubber sheet, 0.140 cm. thick, group 1, $K' = 0.0036$

Ninety-six parts of pale crepe rubber and 4 parts of sulfuric acid were allowed to react. The reaction product was thoroughly washed and then milled to a plastic condition and molded at 140° C. This rubber was very hard and brittle at room temperatures, but plastic at higher temperatures.

Sample 9. Hard Rubber Compound—A vulcanized hard rubber sheet, 0.132 cm. thick, group 1, $K' = 0.0072$

	Per cent
Caucho ball.....	74
Sulfur.....	25
Paraffin.....	1.0

Cured 1.5 hours to 140° C. and 8 hours at 140° C. Free sulfur = 0.36 per cent.

Sample 10. Vulcanized Sulfuric Acid-Treated Rubber—A semi-hard rubber sheet, 0.130 cm. thick, group 2, $K' = 0.0252$

	Per cent		Per cent
Raw rubber.....	46.1	Zinc oxide.....	4.6
Sulfuric acid-treated rubber.....	46.1	Tuads.....	0.4
Sulfur.....	2.8		

Cured 10 minutes at 138° C.

Sample 11. Silica-Filled Insulating Compound¹³—A soft vulcanized filled rubber sheet, 0.127 cm. thick, group 4, $K' = 0.108$

	Per cent		Per cent
Rewashed Riverside smoked sheet.....	49.0	Paraffin.....	1.0
Sulfur.....	2.0	Litharge.....	5.0
Zinc oxide.....	3.0	Silica.....	40.0

Vacuum treatment 8 hours at room temperature and 4 hours at 80° C. Cured 10 minutes to 120° C., 1 hour at 120° C. and 10 minutes blow-off.

Sample 12. Representative "Inner Tube" Stock—A soft vulcanized rubber sheet 0.051 cm. thick, group 3, $K' = 0.0405$

	Per cent		Per cent
Commercial smoked sheet.....	78.4	Zinc oxide.....	7.7
Mineral rubber.....	7.7	Paraffin.....	1.5
Sulfur.....	3.1	Ethylidene aniline.....	1.5

Cured 45 minutes at 143° C.

Sample 13. Commercial Dental Rubber—A sheet of S. S. White's "Buff Rubber Dam," 0.025 cm. thick, group 3, $K' = 0.0243$

Discussion

The data of Figure 5 have been used to calculate an approximate rate of diffusion for each of the thirteen rubbers. These rates are shown by K' in the list of rubbers given above, where K' is the diffusion constant of Equation 5 corrected to a standard thickness of 0.130 cm. by using the inverse square relationship.

Examination of the data shows only one outstanding relation. When the rubber sheets are arranged according to their hardness, they are also very nearly arranged according

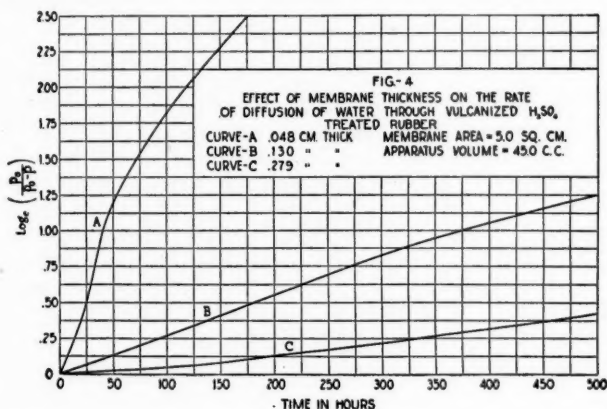
Note—Hardness was judged by stiffness, brittleness, and strength. Permeability was judged from K' , the rate of diffusion for a sheet 0.130 cm. thick.

to their permeability, the hard rubbers being the least permeable. No quantitative relationship was sought, but ac-

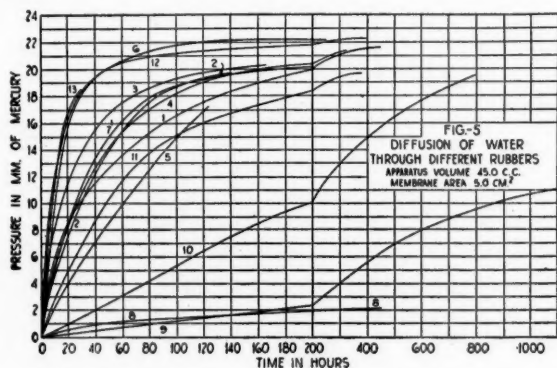
¹² The action of sulfuric acid on rubber is described by Fisher in U. S. Patent No. 1,605,180 (1926).

¹³ The silica filler in this rubber was roasted according to the treatment described by Williams, U. S. Patent No. 1,438,735 (1922).

cording to the degree of hardness and permeability, the thirteen rubbers were divided into five groups: The sulfuric acid-treated rubber and the hard rubber were by far the hardest, being in fact brittle. They were also the least permeable to water. The vulcanized sulfuric acid-treated rubber was semi-hard, tough mechanically, and somewhat more permeable. The third group was composed of the



commercial dental rubber and the representative inner-tube stock, both of which were tougher and stronger and less permeable (allowing for the effect of thickness) than the main body of rubbers—vulcanized pale crepe, vulcanized commercial smoked sheet, vulcanized rewashed smoked sheet, sulfur-rubber compound, low-protein rubber, and silica-filled in-



ulating compound—that formed group 4. (The silica-filled rubber may seem to be out of place in this classification, but as determined by actual handling tests it was found to be softer than the rubbers of group 3.) Group 5 contained only the pure rubber hydrocarbon and the crude raw ribbed smoked sheet, which were the most permeable and the softest.

As composition affects the hardness of a rubber, it obviously plays a role in the diffusion problem. Thus, in general, pale crepe rubber is tougher than smoked sheet and from Figure 5 vulcanized pale crepe (curve 1) was found to be less permeable than vulcanized smoked sheet (curve 2). Rewashing the smoked sheet softens it, indicating the probable cause of the greater permeability shown by curve 3. Other variations in the composition of the rubbers, such as vulcanization, fillers, and low protein content, do not seem to greatly affect the permeability.

The relation between hardness and permeability to water is very useful in explaining other phenomena. A moderate increase in the temperature of a rubber sheet lessens its hardness while at the same time it becomes much more permeable. The increase in permeability is so great that it seems reasonable to believe that part of it may be due to the decrease in hardness. Then again, the loosening in structure, which was described in a preceding paragraph as possibly resulting from the saturation of rubber with water, might, by its softening effect, be the chief cause of the accompanying increase in permeability.

Report of the Raw Rubber Specifications Committee¹

AS INTIMATED in a previous report of the Committee presented at the St. Louis meeting in April, 1928, a temporary procedure was adopted in order to ascertain whether or not the five laboratories represented on the Committee could obtain reasonably comparable stress-strain relationships using the same batch of rubber.

A complete report is appended in which the procedure is outlined and the results of each laboratory are given in considerable detail.

After careful deliberations the Committee has concluded that the testing of raw rubber is not in a very satisfactory state. It therefore makes the following recommendations:

(1) The testing of raw rubber should be made the subject of thorough investigations.

(2) The work should be undertaken by a Physical Testing Committee, preferably under the jurisdiction of the Rubber Division of the AMERICAN CHEMICAL SOCIETY.

The Committee wishes to express its appreciation of the aid given to it by the B. F. Goodrich Company in supplying the broken-down raw rubber employed in these tests.

ELLWOOD B. SPEAR, *Chairman*

C. R. BOGGS

H. L. TRUMBULL

H. E. SIMMONS

N. A. SHEPARD

Method

A batch of pale crepe was broken down on a hot mill by the B. F. Goodrich Company and portions were sent the Firestone,

¹ Presented by the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

Simplex, Akron University, and Thermoatomic laboratories. All laboratories followed the procedure as closely as possible. Goodrich reports using a 600- instead of a 500-gram batch and a higher temperature during the incorporation of the zinc oxide.

Procedure

FIRESTONE FORMULA—The total weight of the batch was 500 grams.

The rubber was cut into slabs about 9 mm. thick and the slabs were cut into strips. Steam was allowed to pass through both rolls in such a manner that a slight hissing sound could be heard at the effluent orifices and a moderate cloud of condensed steam could be seen.

The rolls were opened sufficiently so that the strips of rubber could be joined end to end by a slight squeezing at the overlapped joint as the strips were passed through the rolls once. The long strips thus formed were wrapped around the front roll and allowed to revolve with the roll for 5 minutes. The rolls were then closed little by little so that the rubber was slightly squeezed. As the tightening process was continued the rubber began to spread out somewhat and to decrease in thickness. The squeezing was continued for 2 minutes, at the end of which time the rolls were tightened until a very thin sheet of rubber was formed around the front roll. The rolls were then backed away slowly in order that a continuous sheet of rubber might be formed. Finally the bank was reduced in size until it was approximately 25 mm. in diameter.

The zinc oxide was milled in, the process occupying 3 minutes. The rubber was then cut rapidly back and forth for 5 minutes. During the cutting the steam was turned off the back roll but was allowed to pass through the front roll.

The cutting was done in such a manner that the slit was started at the outer edge of the rubber and continued into approximately the middle of the roll. The end of the rubber thus freed was turned back on the roll so that the outer square corner of the slit was brought into the middle of the roll. This method insures thorough mixing and prevents the formation of pronounced grain.

At the end of the mixing process the rolls were backed away so that the rubber did not touch the back roll, the steam was turned off the front roll, and cold water was allowed to pass through both rolls for 1 minute. The water was then turned off the front roll, but was allowed to pass through the back roll until it was warm but not hot to the hand. The time required was 7 minutes. The mill was, of course, in operation during the cooling period.

The rolls were then tightened until the bank was again about 25 mm. in diameter. The rubber sheet on the front roll was perfectly continuous and smooth. The accelerator and the sulfur were then milled in together, the process occupying 2 minutes.

The rubber was again cut rapidly back and forward for 5 minutes. At the end of this time the rolls were tightened to the required degree and the sheet was cut off the mill in the ordinary manner. The thickness of the sheet should be slightly less than 2.5 mm., if the curing molds are such that the cured sheet is to be approximately 2 mm. thick.

The sheets were cut out the full size of the mold in such a way that the test pieces would be lengthwise around the roll. The raw test sheets, while still warm, were put into a desiccator over calcium chloride and kept there until they were taken out to be put in the press, 2 to 5 hours after milling.

The curing was carried out for the periods indicated on the enclosed sheets. The cured sheets, after removal from the press, were chilled with cold water, cut to size, dried with a cloth, and finally thoroughly dried for a few minutes at a temperature

around 35–40° C. The cured test sheets were then put into the desiccator over calcium chloride and allowed to remain for approximately 20 hours.

The dumbbell pieces were stamped out and prepared in the usual manner for the Scott machine, after which they were returned to the desiccator until they were tested.

Firestone Formula

	Grams	Per Cent
Rubber	470.3	94.06
Zinc oxide	12.5	2.5
D. O. T. G.	2.2	0.44
Sulfur	15.0	3.0
	500.0	100.00

Note 1. The mill on which this was carried out was the ordinary laboratory 30.5 × 15.2 mm. (12 × 6 inches) type. The front roll makes 29 revolutions and the back roll 37 per minute without load.

Note 2. It will be obvious that the time of heating and the time of cooling depend upon the construction of the interior of the rolls, the temperature of the cooling water, and other considerations. Under the conditions described above the rubber was smoothed out into a sheet at 99–100° C., as measured by wrapping four successive pieces of the rubber around a mercury thermometer. If the steam is allowed to escape in a small cloud from each roll, the experimental evidence is that the temperature of the rubber will be approximately the boiling point of water.

Note 3. At the time of the introduction of the sulfur and accelerator, the temperature of the rubber was found to be 71° C. During the mixing period the water was again allowed to run through the front roll for 1 minute and through the back roll continuously. Obviously, the temperature of the rubber will be affected by the temperature of the cooling water and the rate of flow. It was found that the rapid cutting of the rubber tended to lower the temperature slightly. The reading varied from 65° to 70° C.

Note 4. The curing temperature of 137.5° C. was not chosen with malice of forethought. This represented the actual temperature in the curing mold when the thermometer belonged to the press registered 40 pounds (2.8 kg. per sq. cm.) pressure.

RUBBER-SULFUR FORMULA—The rubber, cut in strips, was wrapped around the front roll, while steam was passing through both rolls as described for the Firestone formula. At the end of 5 minutes the rolls were tightened slowly and a sheet was formed around the front roll. The total warming period was 7 minutes. The rolls were then backed away slowly until a con-

Rubber-Sulfur Formula

Rubber	92.5
Sulfur	7.5
	100.0

Maxima and Minima

(Five laboratories; seven tests; Firestone formula)

	MAXIMA	MINIMA
45-MINUTE CURE		
Tensile at 700 per cent elongation	124	72.3
Tensile at break	229	174
Per cent stretch at break	850	775
60-MINUTE CURE		
Tensile at 700 per cent elongation	169	108
Tensile at break	238	197
Per cent stretch at break	823	737
75-MINUTE CURE^a		
Tensile at 700 per cent elongation	191	135
Tensile at break	265	204
Per cent stretch at break	781	696
90-MINUTE CURE		
Tensile at 700 per cent elongation	218	152
Tensile at break	269	214
Per cent stretch at break	784	703

^a Thermatomic Test No. 1, 75-minute cure omitted.

Summary of Tests Using Goodrich Rubber and Firestone Formula
(Curing temperature, 137.4-137.7° C.)

	GOOD- RICH	SIM- FLEX	SIM- MONS	FIRESTONE		THERMATOMIC		REMARKS
				Run I	Run II	Run I	Run II	
Tensile ^a at 700 per cent elongation	119	112	108	80	123	72.5	100	Goodrich testing temperature 23.3° C.
Tensile ^a at break	215	206	213	174	192	189	229	Simplex testing temperature 22.2° C.
Per cent stretch at break	798	791	803	838	775	850	830	
Tensile at 700 per cent elongation	155	151	141	112	169	108	122	Simmons testing temperature 23.3° C.
Tensile at break	233	229	238	197	209	238	223	Thermatomic, Run I, testing temperature 26.7° C.
Per cent stretch at break	783	775	790	790	737	823	806	Thermatomic, Run II, testing temperature 26.1° C.
Tensile at 700 per cent elongation	191	183	166	135	202	75 ^{b,c}	171	Thermatomic, Run I, tested March 29, 1928
Tensile at break	248	244	265	204	214	226 ^b	255	
Per cent stretch at break	753	753	781	768	696	807 ^b	756	
Tensile at 700 per cent elongation	218	209	190	162	213	152	187	Thermatomic, Run II, tested June 22, 1928
Tensile at break	253	242	269	213	217	264	267	
Per cent stretch at break	727	723	755	740	703	784	760	

^a Tensiles are expressed in kilograms per square centimeter.

^b Obviously wrong, because it is inconsistent with other cures on same stock.

^c Error in transcribing. Correct figure is 117.

tinuous sheet of rubber was formed and the bank had become about 25 mm. in diameter. The sulfur was milled in and the sheet cut rapidly back and forth for 5 minutes, the steam having been cut off the back roll in the meantime. The rolls were then tightened until a sheet of the desired thickness was formed, after which the batch was cut off the mill in the usual manner.

The conditioning, curing, and testing were carried out according to the procedure described for the Firestone formula.

Summary of Tests Using Goodrich Rubber and Rubber-Sulfur Formula

	FIRESTONE	SIMPLEX	THERM-ATOMIC
Curing temperature	141° C.	141° C.	141° C.
Testing temperature	26.1° C.	22.2° C.	26.4° C.
150-MINUTE CURE			
Tensile at 500 per cent elongation	15.6	12.7	14.5
Tensile at 800 per cent elongation	54.5	52.3	61.2
Tensile at break	128	142	141
Per cent stretch at break	947	963	955
180-MINUTE CURE			
Tensile at 500 per cent elongation	16.9	20	16.9
Tensile at 800 per cent elongation	71.8	70	76
Tensile at break	135	142	181
Per cent stretch at break	906	915	927
210-MINUTE CURE			
Tensile at 500 per cent elongation	18.6	22.9	18.4
Tensile at 800 per cent elongation	83	81	89.4
Tensile at break	151	131	163
Per cent stretch at break	894	878	895